DEGRADATION KINETICS OF ORGANIC AMINES

IN SUPERCRITICAL WATER

By

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IN SUPERCRITICAL WATER

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NOMENCLATURE

Symbols

1^o	Primary
2^o	Secondary
3^o	Tertiary
C_0, $C_{n,0}$	Initial concentrations of reactive species (mol l^{-1})
C_A	Concentration of species A (mol l^{-1})
C_P	Thermal conductivity ($Wm^{-1}K^{-1}$)
k'	Pseudo first order rate constant
$K^{\ddagger}$	Equilibrium constant of transition state species
k_0	Reference state rate constant
K_a	Equilibrium dissociation constant of acid in aqueous solution
K_b	Equilibrium dissociation constant of base in aqueous solution
K_W	Ion product of water (mol^2 kg^{-2})
P_C	Critical point pressure (22.05 MPa)
pK_a	Negative logarithm of acid dissociation constant
pK_b	Negative logarithm of base dissociation constant
P_r	Reduced pressure
r_i	Molecular/complex radius of species i (cm)
S_N1	Unimolecular nucleophilic substitution mechanism
S_N2	Bimolecular nucleophilic substitution mechanism
T_C	Critical point temperature (374 ^oC)
T_r	Reduced temperature
$X^{\ddagger}$	Transition state species
Y_n	Yield of species n
$\Delta G^{\ddagger}$	Free energy of activation (kJ mol^{-1})
$\Delta v^{\ddagger}$	Activation volume (cm^{-3} mol^{-1})
ε	Dielectric constant of water
κ	Transmission coefficient
κ_T	Isothermal compressibility
μ_i	Dipole moment of species I (Debye, D)
ρ	Solvent density (kg m^{-3})
$\rho_{r,w}$	Reduced water density
ρ_w	Water density (kg m^{-3})
Ψ	Modified rate constant

Abbreviations

2, 6-DNA	2, 6-dinitroaniline
2NA	2-nitroaniline
2NPDA	2-nitro- 1, 4-phenylenediamine
3NPDA	3-nitro- 1, 2-phenylenediamine
4NA	4-nitroaniline
4NPDA	4-nitro- 1, 2-phenylenediamine
AVT	All Volatile Treatment
BA	Benzylamine
BP	Boiling Point
BPA	Benzylphenylamine
DOE	Department of Energy
DR	Distribution Ratio
FA	Film forming Amine
IC	Inter-granular Corrosion
I-NERI	International Nuclear Energy Research Initiative
LWR	Light Water Reactor
MPa	Mega Pascal
NA	Neutralizing Amine
NERI	Nuclear Energy Research Initiative
NIST	National Institute of Standards and Technology
OT	Oxygenated Treatment
PC	Pitting Corrosion
Ph	Phenol
PWR	Pressurized Water Reactor
SCC	Stress Corrosion Cracking
SCWO	Supercritical Water Oxidation
SCWR	Supercritical Water Cooled Reactor
SFE	Supercritical Fluid Extraction
THQ	1, 2, 3, 4-tetrahydroquinoline

Other

E	Activation energy (kJ mol^{-1})
F	Fractional conversion
h	Plank’s constant
K	Kelvin
k	Rate constant
N	Avogadro number (6.022E23 mol^{-1})
^{o}C	Degree centigrade
P	Pressure
R	Gas constant (J mol^{-1} K^{-1})
T	Temperature
t	Time (s)

CHAPTER – I

INTRODUCTION

One of the major requirements for sustaining human progress is an adequate source of energy. The largest sources of energy currently are combustion of coal, oil and natural gas. These will last quite a while, but probably will run out or become limiting in tens to hundreds of years. Solar energy is viable but is not developed except for special applications due to high cost. Nuclear energy is likely to remain cheaper than oil and gas. The main advantage of nuclear and solar energy is that it does not put carbon dioxide into the atmosphere.

To enhance the role of nuclear energy systems, the government of the United States of America began two programs; Nuclear Energy Research Initiative (NERI) in 1999 and International Nuclear Energy Research Initiative (I-NERI) in 2001 [1]. The objective of these two programs is to develop safe, clean, sustainable and cost-effective nuclear energy systems that can fuel the world for future generations. In April 2003, the Department of Energy (DOE) developed a concrete plan for development of such systems and issued ‘A Technology Roadmap for Generation IV Nuclear Energy Systems’ [2]. The supercritical water-cooled reactor (SCWR) is one of the six reactor technologies selected for research and development under the Generation IV program.

At present there are 103 commercial nuclear reactors with operating licenses in the United States. These are located at 64 different sites in 31 states, 34 of which are

Boiling Light Water Reactors (LWRs) and 69 are Pressurized Water Reactors (PWRs). About 20% of the electricity generated in United States is from nuclear and this energy is considered emission free [3, 4]. The working principle of LWRs is similar to conventional coal fired power plant except that fuel source (combustion of coal) is replaced by nuclear fuel. PWRs operation is carried out in two different loops, primary and secondary. Primary loop consists of working fluid (water) in direct contact with nuclear fuel and is heated by radioactive decay of the nuclear fuel. Water in the primary loop is under high pressure to prevent it from boiling. Heat from the primary loop is transferred to the secondary loop to generate steam which is used to propel turbines. Use of a two loop system prevents leakage of radiation emitted in the primary loop to other steam generation equipment. In contrast, Supercritical Water Cooled Reactor (SCWR) can be visualized as LWR operating above the thermodynamic critical point of water [5, 6].

Supercritical Water-Cooled Reactor (SCWR)

SCWRs are high temperature, high pressure water cooled reactors that operate above the critical point of water (374 ^{o}C, 22.1 MPa). SCWR has the following advantages over the current state of art nuclear Light Water Reactors (LWRs) [5-7]:

1. The thermal efficiency of SCWRs can be much higher compared to LWRs. The efficiency of SCWR can approach 44%, compared to 33-35% for LWRs.
2. The mass flow rate of coolant per unit core thermal power is low in SCWRs. This results in increased enthalpy of coolant offering reduction in size of reactor coolant pumps, piping, pumping power and associated equipment.

3. Reduced coolant flow rate results from once-through coolant path in the reactor vessel and reduced coolant density.
4. Discontinuous heat transfer regimes in the reactor core are eliminated as a result of single phase operation (no boiling).
5. Steam dryers, steam separators, recirculation pumps and steam generators which are currently used in LWRs are not required. This results in simplified plant operation with fewer major components.

Few data exist on the behavior of materials in a supercritical water environment under irradiation. Water chemistry is one of the key issues addressed by the DOE in the research and development of SCWR as it may lead to corrosion of materials of construction. DOE plans to develop a pilot plant scale supercritical water cooled reactor by the year 2020 [2].

Current status of research

At present, no pilot plant scale reactor is available for design evaluation and analysis of SCWR. The technology available for LWRs and supercritical water cooled fossil-fired power plants is considered basic technology for development of SCWR. It can be said that current status of research in the development of SCWR is at a rudimentary stage of testing materials of construction and analyzing the feasibility of reactor operation [8]. According to 2004 NERI annual report published by DOE, current research for SCWR is classified into three major goals [6]:

1. Fuel-cycle neutronic analysis and reactor core design,

2. Fuel cladding and structural material corrosion and stress corrosion cracking studies, and
3. Plant engineering and reactor safety analysis.

The issue of water chemistry is addressed under fuel cladding and structural material corrosion and stress corrosion cracking studies. Water chemistry at supercritical conditions poses significant challenges in the research and development of SCWR as reactor material is susceptible to corrosion under continuous operation.

Water chemistry and corrosion

In any hydrothermal system, water treatment is critical to both equipment life and efficiency. Most of the conventional hydrothermal systems operating under sub-critical conditions use stainless steel or metal alloys with Iron (Fe) and Copper (Cu) as equipment material [9]. Poor control of alkalinity / acidity of water and presence of impurities in feed water in such systems may lead to various forms of corrosion. Corrosion results in damage to piping and equipment as well as loss of high quality water and energy. In some instances, the products of corrosion, if returned to the boiler (or heating unit), may contribute to the formation of damaging deposits over the unit internals there by reducing the overall system reliability and increasing the operating and maintenance costs. Different forms of corrosion include pitting corrosion (PC), general corrosion, inter-granular corrosion or inter-crystalline corrosion (IC) and stress corrosion cracking (SCC).

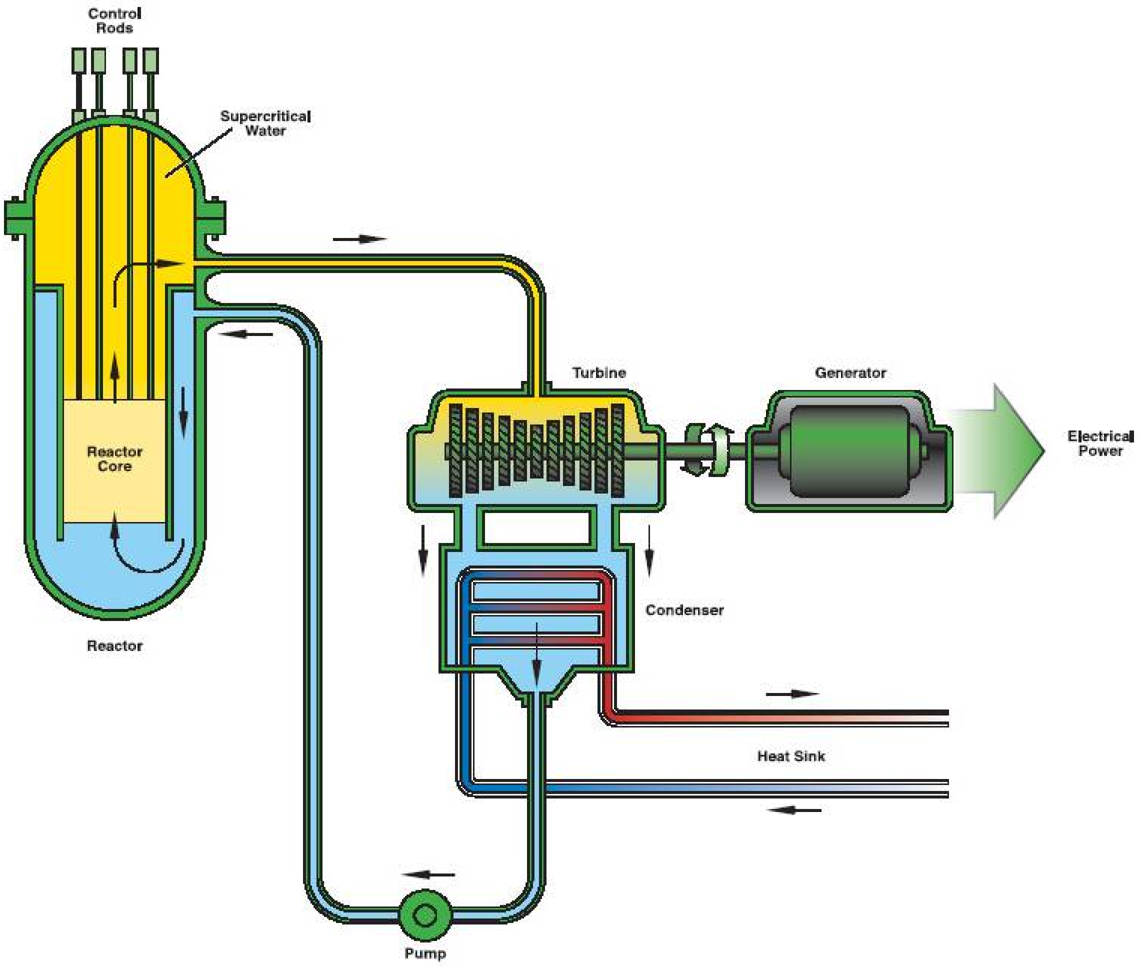

Figure 1.1 Schematic of Supercritical Water Cooled Reactor [2]

Water chemistry control – focus on pH

The fundamental objectives of feed-water chemistry in a hydrothermal system are control over acidity / alkalinity and impurities to reduce corrosion of material of construction. Currently there are three types of chemical treatments available for control over acidity / alkalinity in hydrothermal systems operating at sub-critical conditions [9, 10]:

- Type I is classical all-volatile treatment (AVT) using ammonia (NH_3) and a reducing agent or oxygen scavenger (such as hydrazine)
- Type II is the same as Type A minus the reducing agent, called new AVT
- Type III is oxygenated treatment (OT) using only ammonia and oxygen (O_2)

All three treatments mentioned involve addition of an external chemical agent to feedwater to maintain the required minimum pH at process operating conditions. The major difference between the three types of treatments is that Type I provides a reducing environment, whereas Types II and III result in oxidizing environments. In nuclear pressurized water reactor (PWR) plants, the feed water treatment is limited to all-volatile treatment as the secondary cycle corrosion is extremely pH sensitive [11]. In Type III treatment, there is a possibility of reaction between ammonia and oxygen resulting in consumption of ammonia which further results in shift of pH value from alkaline to acidic scale. Hence Type III treatment is least preferred compared to Type I and Type II. All the three treatments are currently used in steam generation systems depending on the type of impurities present in the feed water and other pH control considerations. However, it should be noted that these treatments can be used when process operating conditions are in the sub-critical region. The application of above treatments may not be effective in stabilizing the pH and further reducing the corrosion in hydrothermal systems operating above the critical point.

Organic amines have been used extensively as pH stabilizing agents in all-volatile treatments in various boiler feed water and steam condensate systems -- replacing ammonia [12-24]. Amines offer unique advantages over ammonia like low volatility, varying distribution ratios and ease of shipping and handling. Moreover ammonia is not suited for this application as pH neutralizing agent in water at near critical operating conditions. This is because in sub-critical once-through reactors, the presence of NH_3 / O_2 does not cause problems, since oxidation of ammonia is slow. In contrast, the oxidation rate of ammonia is strongly accelerated near supercritical conditions with major oxidation products being nitrogen (N_2) gas and N_2O. These oxidation reactions lead to ammonia and oxygen consumption resulting in a shift of pH to less alkaline values [9, 11].

Proposed work

In view of current progress in research and development of SCWR and its unique advantages over existing electricity generation units, advanced research on water chemistry is necessary. This report evaluates the feasibility of application of organic amines as acid neutralizing agents in hydrothermal systems operating above the thermodynamic critical point of water.

Hypothesis

Based on the proven performance of organic amines in sub and near-critical hydrothermal systems as acid neutralizing agents, it is hypothesized that organic amines have the potential to remain relatively stable and elevate pH to required alkaline values at conditions above the critical point. Organic amines that stabilize pH decompose into light molecular weight organic and inorganic molecules. Initial review of the literature indicates that the rate of decomposition of an organic amine in any hydrothermal system is mainly dependent upon process operating temperature and pressure. Two major mechanisms for amine decomposition in supercritical water are identified: pyrolysis and hydrolysis. Pyrolysis is dominant in low water density region and hydrolysis in high water density region. There exists a range of solvent density where the two mechanisms proceed in parallel.

In the case of supercritical water, the rate of decomposition of an organic amine is not only dependent upon the operating temperature and pressure but also on solvent properties in hydrolysis region (higher water densities). Better prediction of rates of decomposition of amines under hydrolysis can be obtained by correlating the solvent properties (di-electric constant, density and ionic product) with the decomposition reaction rate constant.

Objectives

1. To understand and analyze the properties of water at supercritical conditions,
2. To assess the work that was done on decomposition kinetics of amines in water at supercritical conditions,

3. To draw analogies between mechanisms at sub-critical and supercritical conditions for structurally similar organic compounds and address key issues related to solvent effects on reaction kinetics, and
4. To recommend feasible methodology for generation of kinetics data and development of mechanistic models.

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CHAPTER - II

PROPERTIES OF SUPERCRITICAL WATER

In this chapter thermo-physical properties of supercritical water will be discussed. A fluid is termed as supercritical when its temperature and pressure exceed the critical temperature and pressure, respectively. For water (H_2O), the critical temperature is T_C 374°C and critical pressure is P_C = 22.05 MPa. At this temperature and pressure, the properties of vapor and liquid cannot be distinguished. The phase diagram of a single component fluid is shown in Figure 2.1. The vapor liquid saturation curve disappears beyond the critical point indicating that the vapor and liquid phases coexist. Any liquid when heated at constant pressure beyond its critical pressure would undergo expansion

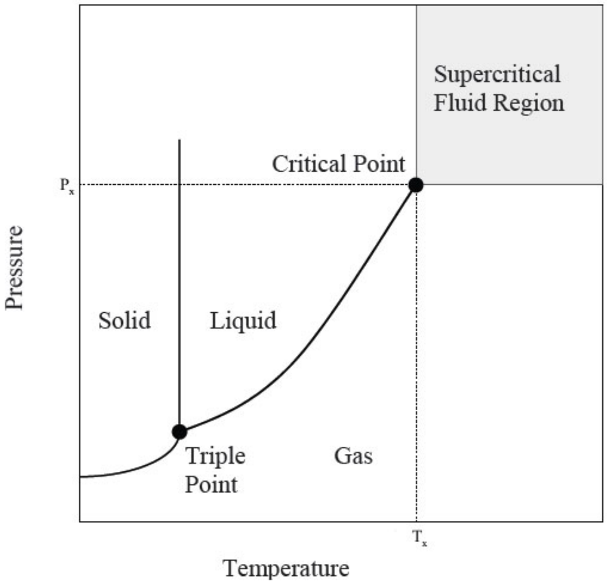

Figure 2.1 Phase diagram for single component

reaching a vapor like state without phase transition. This physical phenomenon is termed as continuity of states. At any temperature beyond the critical point, the vapor can no longer be liquefied regardless of the pressure applied.

Properties of supercritical water

Properties of supercritical water are quite different from those of liquid water at ambient conditions. Water at supercritical conditions has unique properties, some are intermediate of vapor and liquid (viscosity, dielectric constant) and some are not (C_P, thermal conductivity) [1]. This section briefly describes the thermo physical properties of supercritical water.

Density

Figure 2.2 shows the isothermal variation of density with pressure [2]. It can be observed that the density in near critical region (below 22.05 MPa, vapor) changes rapidly with very slight increase in pressure. This change in pressure shifts the density to liquid like values. At this point, the fluid can be visualized as a dense gas with density comparable to liquids. Note that the drop shifts towards higher temperatures at higher pressures. In the following sections it will be shown that other physical properties like viscosity and specific heat follow a smooth trend with density even in the critical point region.

Viscosity

Figure 2.3 shows the isothermal variation of viscosity at different temperatures [2]. As in the case of density, there is a sharp change in viscosity near supercritical point (Figure 2.3 A). This difference is due to diverging compressibility at critical point

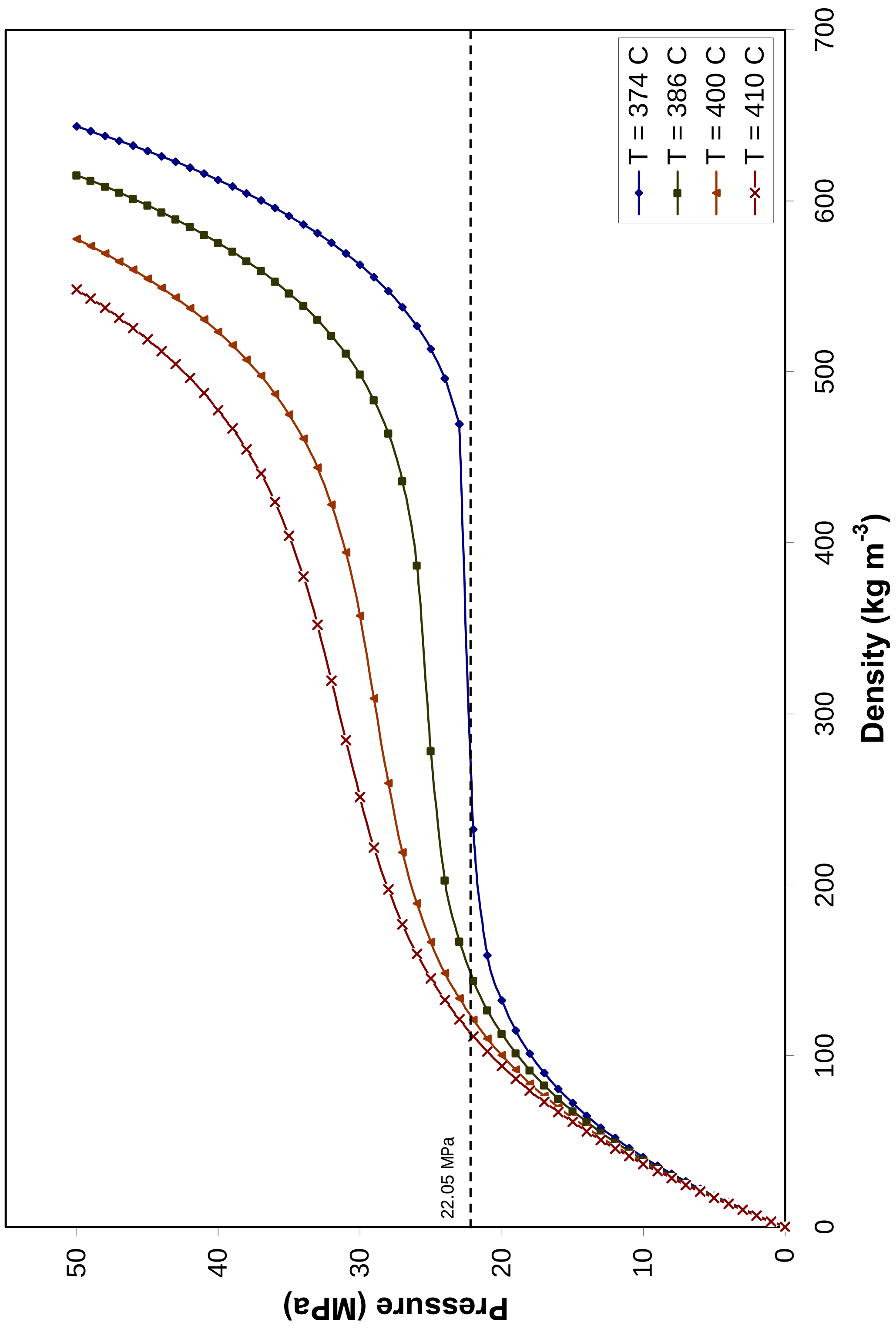

Figure 2.2 Isothermal variation of density with pressure [NIST database. Ref. 2]

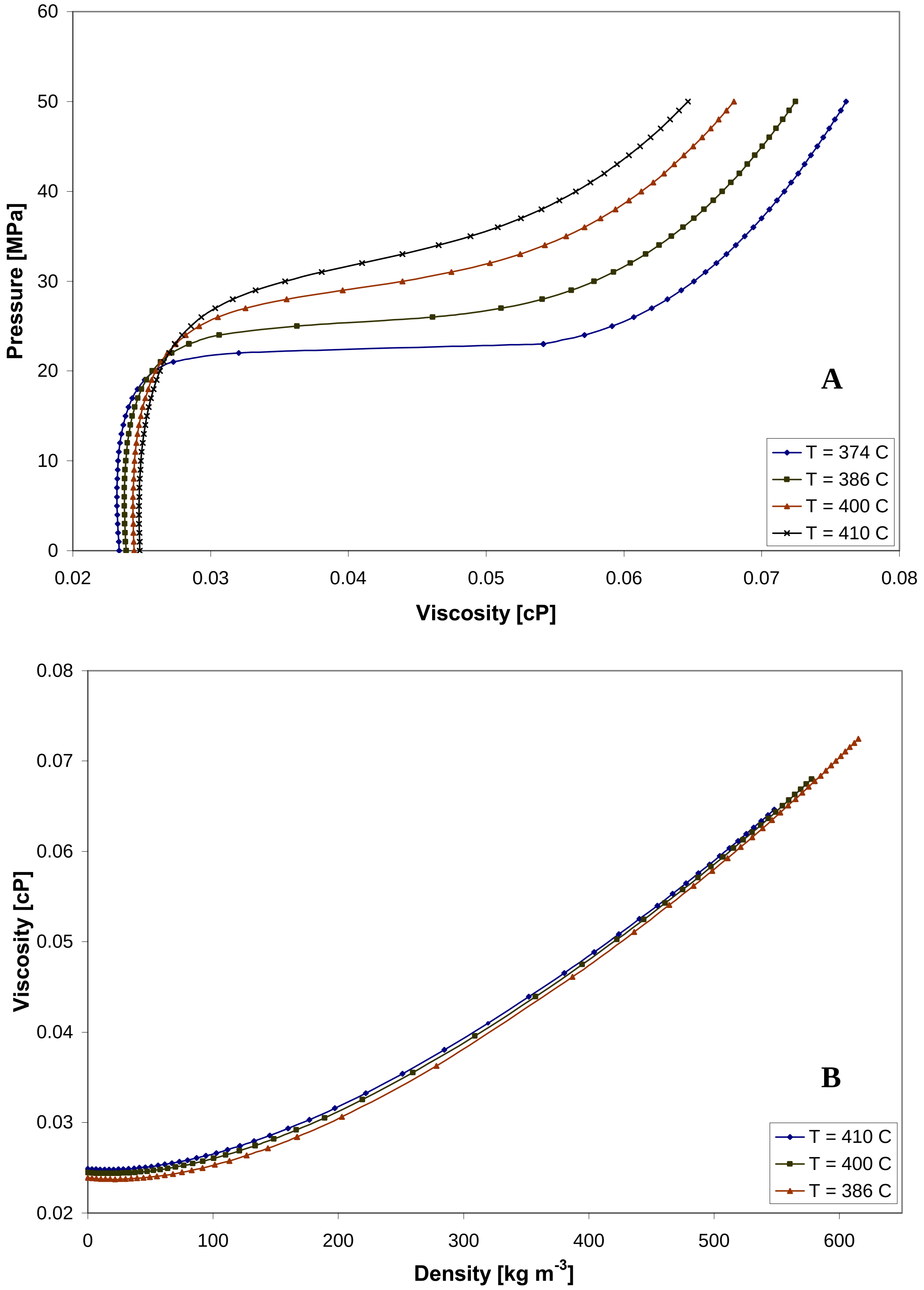

Figure 2.3 (A) Isothermal variation of viscosity with pressure. (B) Isothermal variation of viscosity with density [NIST database, Ref. 2]

of water. When viscosity is plotted against density along the same isotherm there are no sharp changes in the values viscosity of irrespective of critical point region (Figure 2.3 B). Viscosity of supercritical water is far less than ambient water making it a fluid with high self diffusivity at elevated temperatures [3-7]. This property of supercritical water is considered as great advantage for its use in process industries

Dielectric constant

Dielectric constant (ε) or permittivity is defined as a numerical quantity that expresses the degree of non-conductivity of a substance (Dielectric constant of vacuum = 1.0). In Figure 2.4, ε of water is plotted against temperature (left y – axis) and density (right y – axis) [8]. Notice the steep change in the value of ε from 13.2 to 2.6 with change in temperature near critical region. At these conditions water is a low dielectric fluid, a poor solvent for electrolytes and a good solvent for organic compounds. This sudden drop in ε change is due to the diverging expansion coefficient [1]. When the same isobar is plotted against density, the steep change is replaced by a smooth curve following similar trend as viscosity plotted against density (Fig 1.3 B).

The properties, viscosity, ε, coefficient of self diffusion, enthalpy and entropy are intermediate between those of vapor and liquid and can be tuned to desired value by changing density of water above critical point.

Beyond critical the point, properties such as heat capacity, isothermal compressibility and isobaric coefficient do not behave smoothly with density and cannot be considered intermediate between those of liquid and vapor. The following section discusses the isobaric variation of heat capacity at constant pressure near critical region.

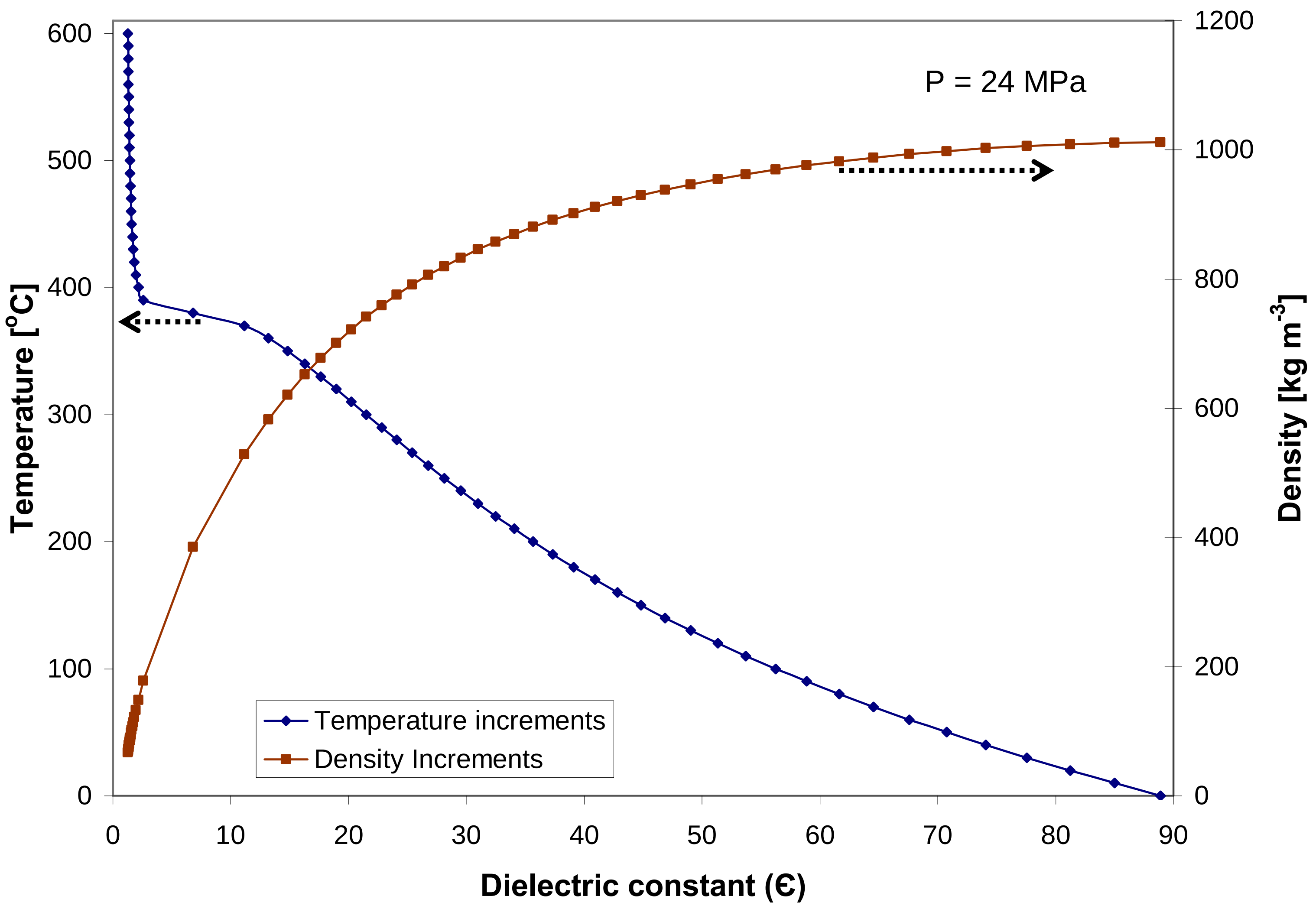

Figure 2.4 Dielectric constant isobar of water plotted against temperature and density [Ref. 8]

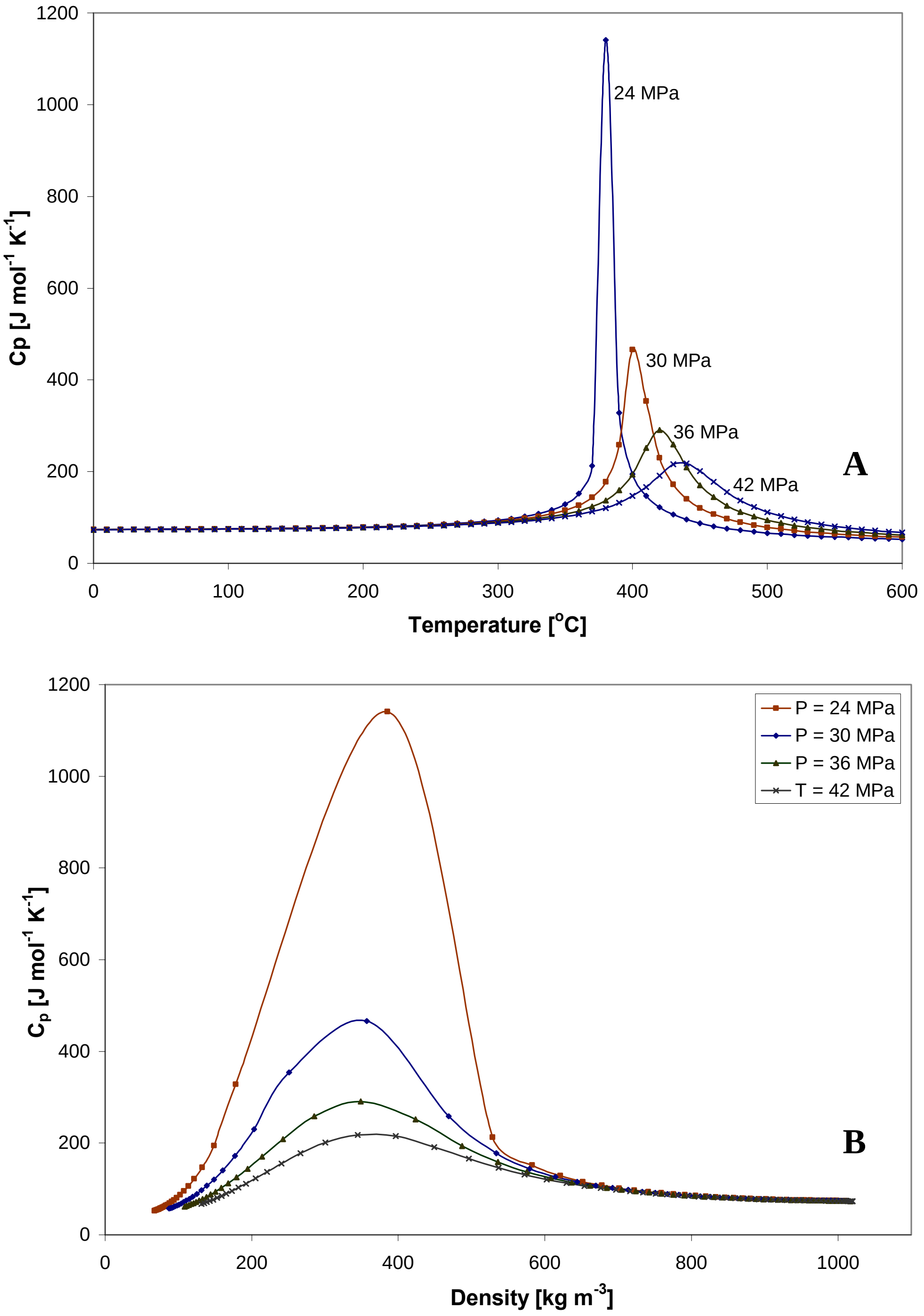

Figure 2.5 (A) Isobaric variation of C_P with temperature. (B) Isobaric variation of C_P with density [NIST database Ref. 2]

Heat capacity (C_P)

Isobaric variation of C_P is plotted against temperature and density in Figures 2.5 A and B respectively [2]. The sharp spike (24 MPa) in Figure 2.5 (A) is equivalent to the broad spectrum (24 MPa) in Figure 2.5(B). This is because a small change in temperature causes a huge density change due to diverging expansion coefficient [1].

Ionic product (K_w)

Ionic product of water is defined as the product of hydrogen ion concentration and hydroxide ion concentration. At ambient temperature $K_w = 1.0 \times 10^{-14}$ mol^{-2} l^{-2}. Figure 2.7 shows ion product and density plotted against temperature (isobars) [2] and Figure 2.8 shows ionic product of high-temperature water and steam versus temperature [9]. Steam and low-density supercritical water behave like non-polar solvents. At low pressures, water behaves as a non-polar solvent with low self-disassociation. High pressures can increase the ionic product to values above those found for water at ambient conditions. Ion product can significantly alter reaction mechanisms in supercritical water as the concentration of H^+ and OH^- ions is sensitive to conditions of operation.

Hydrogen bonding

Few hydrogen bonds exist in supercritical water compared to ambient liquid water. It has also been reported that almost all the properties of supercritical water differ from ambient water due to the decrease in number of hydrogen bonds as supercritical state is reached [10]. Unlike continuous network of hydrogen bonds in ambient liquid water, hydrogen bond network in supercritical water exists as clusters. The size of cluster depends on the localized state in any supercritical water system and is a function of pressure and temperature [11-14].

It has been observed that sudden change in physical properties at the critical point makes water a highly corrosive fluid in supercritical water systems [15]. These properties include density, pH value, and electrochemical potential of the solution. The temperature plays an important role influencing the aggressiveness of attacking solvent species to accelerate corrosion. The investigation of chemistry of organic amines in this region is of fundamental interest.

The data used to generate various plots in this chapter are attached in Appendix A.

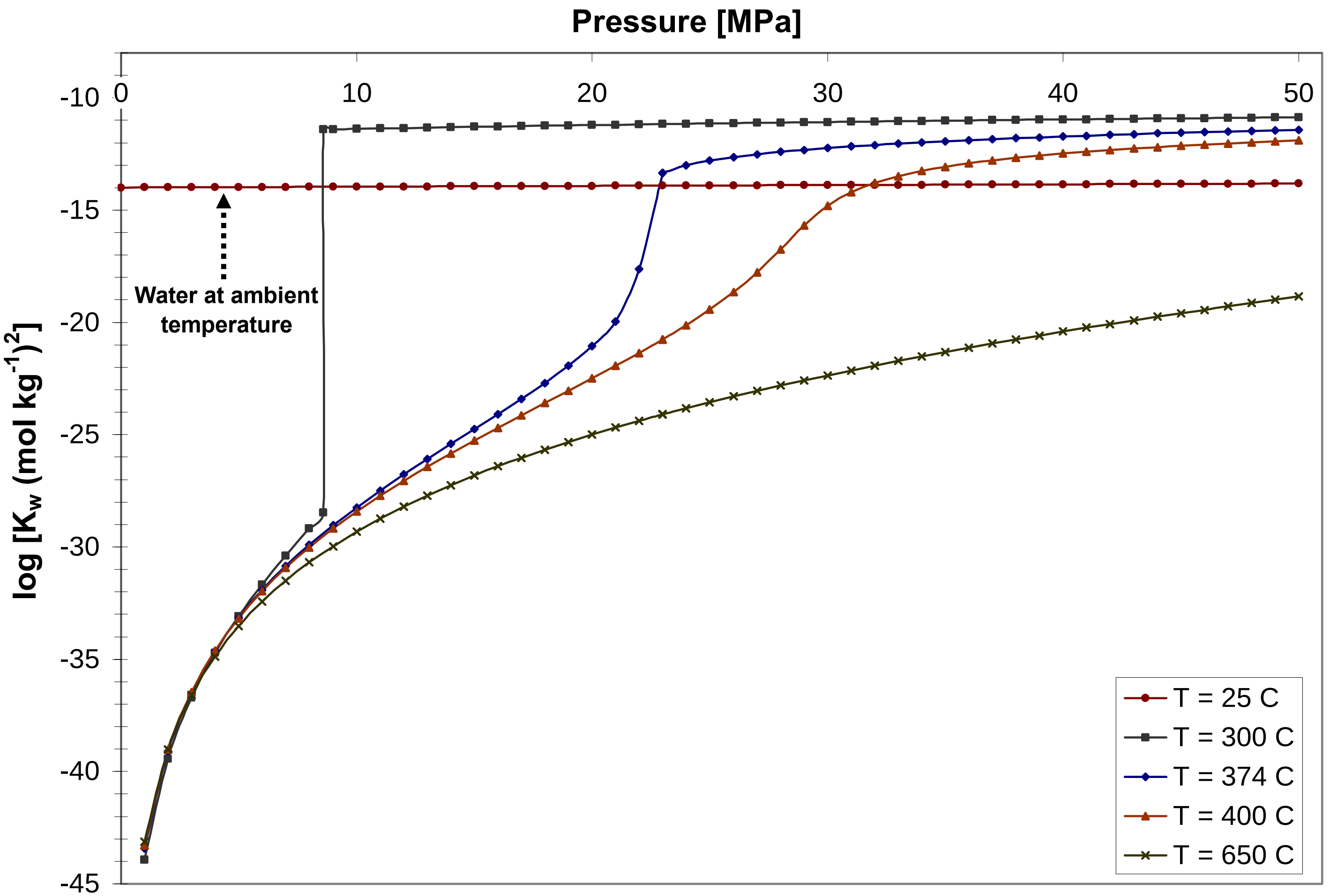

Figure 2.7 Isothermal variation of ion product of water [Ref. 9]

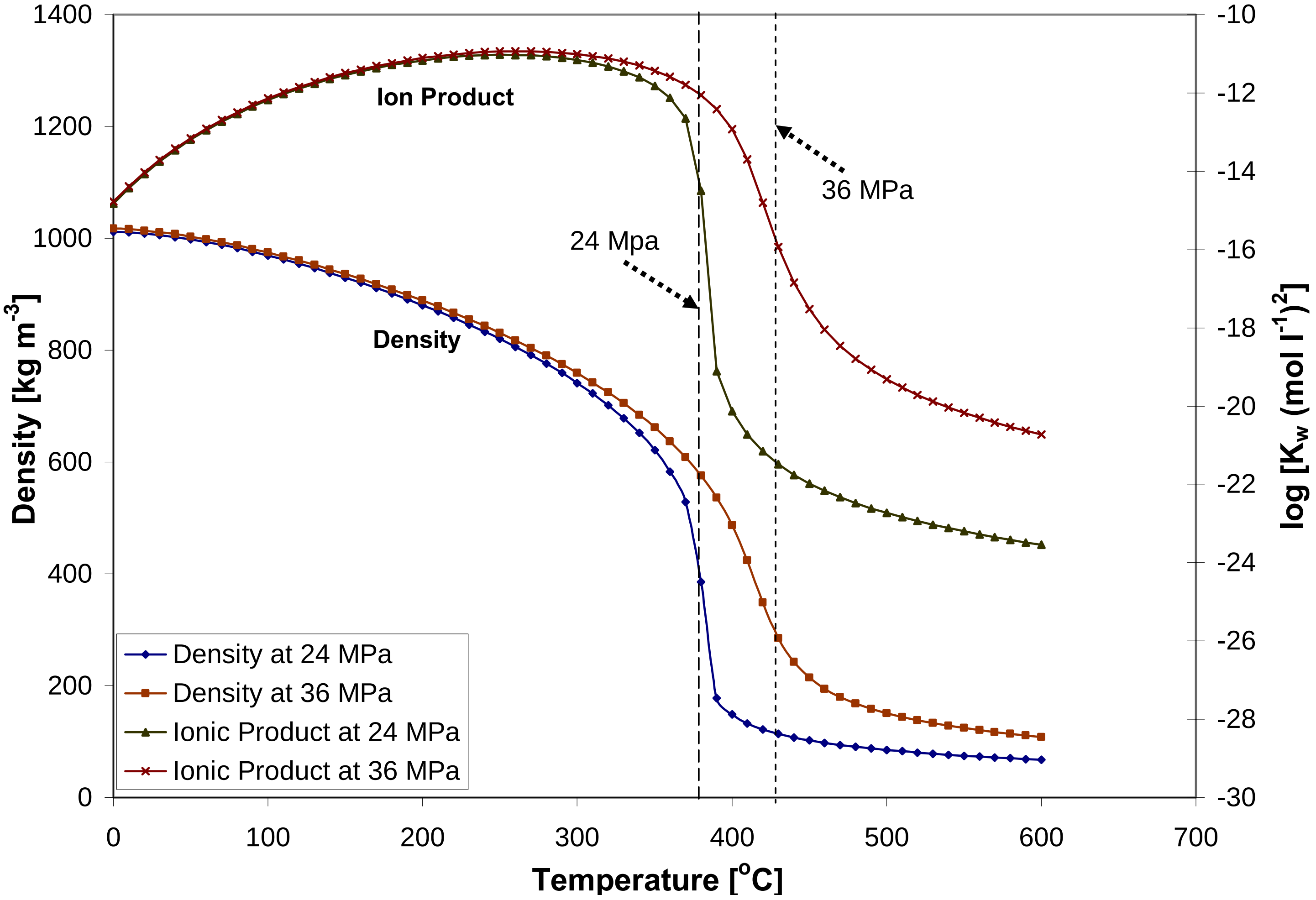

Figure 2.7 Density and Ionic product isobars of water plotted against temperature [Ref. 2 & 9]

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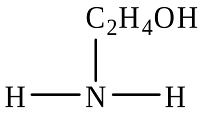
CHAPTER – III

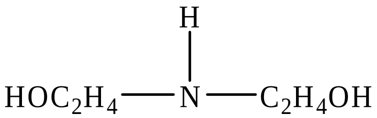
ORGANIC AMINES AS ACID NEUTRALIZING AGENTS

Amines are nitrogen-containing in which one or more of the hydrogens has been replaced by an alkyl or aryl group. Amines are as broadly classified as primary (1^o), secondary (2^o) and tertiary (3^o) amines based on number of alkyl (or aryl) groups attached to nitrogen atom.



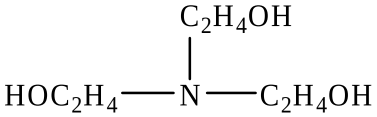
$$H - \overset{C_2H_4OH}{\overset{|}{N}} - H$$

Figure 3.1 (a) Monoethanolamine (1^o – amine)



$$HOC_2H_4 - \overset{H}{\overset{|}{N}} - C_2H_4OH$$

Figure 3.1 (b) Diethanolamine (2^o – amine)



$$HOC_2H_4 - \overset{C_2H_4OH}{\overset{|}{N}} - C_2H_4OH$$

Figure 3.1 (c) Triethanolamine (3^o - amine)

Like ammonia, most amines are Brønsted or Lewis bases. The basicity of amines will be discussed in later sections of the chapter. Amines are widely used in commercial hydrothermal systems as acid neutralizing agents and corrosion inhibitors. They have been proven to be very effective in stabilizing pH of high temperature water in boiler and steam condensate systems [1-3].

Amines are broadly classified at the industrial scale as acid neutralizing amines (in short NA) and film forming amines (in short FA) in their application as corrosion inhibitors [4]. A corrosion inhibitor is defined as a chemical substance which, when added in small concentrations, effectively checks, decreases, or prevents the reaction of a metal with the environment. Acid neutralizing amines or alkalizing amines or volatile amines are used to elevate the pH of water environment by neutralizing H^+ ion concentration. Film forming amines are aliphatic amines with a long hydrocarbon chain which, may deposit on inner surfaces of metallic systems in which circulates liquid water, forms a protecting film against aggressive corrosion causing chemicals. Numerous NA-amines are being used as pH neutralizing and elevation agents at industrial scale. The selection of appropriate amine is based on its basicity, volatility and stability [5].

Basicity of Amines

Like ammonia, amines are Brønsted or Lewis (nucleophiles) bases. The better competitor the amine is in the proton-transfer reaction, the stronger is Brønsted basicity. It is common to compare basicities quantitatively by using pK_a's of their conjugate acids (ammonium ion) rather than pK_b's. If ammonium ion is a stronger acid, the related amine must be a weak base. If it is easy to remove a proton from the ammonium ion to give the amine, the amine itself must be a poor competitor in the proton-transfer reaction.

Strongly basic amines give ammonium ions from which it is difficult to remove a proton, ammonium ions with high pK_a values [6].

Hydrogen bonding

Structure of organic amines has significant influence on their ability to accept a proton in aqueous solutions. In other words the basicity of amine is a factor of the structure of amine in aqueous solutions [7]. In general, the more substituted an ammonium ion, the more stable it is. The more stable an ammonium ion, the less readily it loses a proton, and the higher its pK_a. pK_a values of some simple amines in aqueous solutions at 25^oC and 1Atm are listed in Table 3.1. The general trend of pK_a values on the left hand and right hand sides of the table can be explained by concept of hydrogen bonding. It can be observed that di-methylamine is a stronger base than methylamine; which is, in turn, a stronger base than tri-methylamine. This trend is not observed in case of ethanolamine in which di-ethanolamine is weaker base than mono-ethanolamine. Things are totally different with pK_a values of amines in gas phase.

Table 3.1 pK_a values for some simple amines in aqueous solutions at 25^oC and 1 Atm [8]

Compound	**pK_a**		**Compound**	**pK_a**
Methylamine	10.66 ± 0.20	Primary (1^o)	Ethanolamine	9.16 ± 0.20
Di-methylamine	10.73 ± 0.20	Secondary (2^o)	Di-ethanolamine	8.71 ± 0.20
Tri-methylamine	9.75 ± 0.20	Tertiary (3^o)	Tri-ethanolamine	7.77 ± 0.10

In gas-phase, order of increasing pK_a is $^+NH_4 < ^+NRH_3 < ^+NR_2H_2 < ^+NR_3H$. The irregularities of the values in aqueous solutions can be explained by the concept of hydrogen bonding. Ions in solution are strongly stabilized by solvation, by interaction of the solvent molecules with the ion [7]. One such interaction is the formation of partial covalent bond due to strong dipole - dipole attractions as in hydrogen bonding. An alkyl group has two different effects on ammonium ion stability in aqueous solutions. One effect is the stabilizing effect and other, destabilizing. An alkyl group stabilizes the ammonium ion by dispersing the charge and simultaneously destabilizes the ion by interfering with solvation. In case of primary amines, two hydrogen bonds are formed between two available hydrogens and water. In addition to this, stabilizing effect of alkyl group predominates the destabilizing effect making it a strong base. In case of secondary amines, the destabilizing effect is almost balanced by stabilizing effect. But in tertiary amines, the presence of three alkyl groups makes the ammonium ion more unstable and hence the result is a less stable, more acidic ammonium ion.

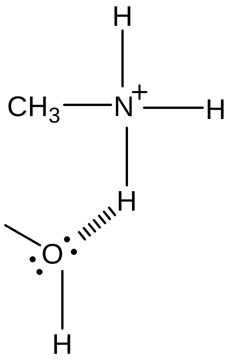


Figure 3.2 Stabilization of methyl group on ammonium ion through hydrogen bonding

In gas phase, where there is no solvation, only the stabilizing effects remain, and each replacement of hydrogen with an alkyl group makes the ammonium ion more stable.

Aromaticity and hybridization

Aromatic (or aryl-) amines are weaker bases than aliphatic amines due to the resonance delocalization of lone pair of electron on nitrogen. Hybridization also has significant effect on basicity of aromatic amines. The greater the percentage of s-character, the closer the lon pair of electrons to nitrogen nucleus which results in decreased ability to participate in proton transfer reaction. Very few aromatic amines are used at industrial scale as corrosion inhibitors. pK_a values of some simple aromatic amines in aqueous solutions at 25^{o}C and 1 atm are tabulated in Table 3.2. Resonance delocalization of electron pair in aniline is illustrated in Figure 3.3. Hybridization of nitrogen atom in aniline is some where in between sp^2 and sp^3. Delocalization of electron pair combined with high s-character results in low basicity of aniline [9]. In di-phenylamine two benzene rings replace two hydrogens bonded to nitrogen atom making it a much weaker base than aniline. This is due to the increase in degree of delocalization of lone pair of electrons on nitrogen atom.

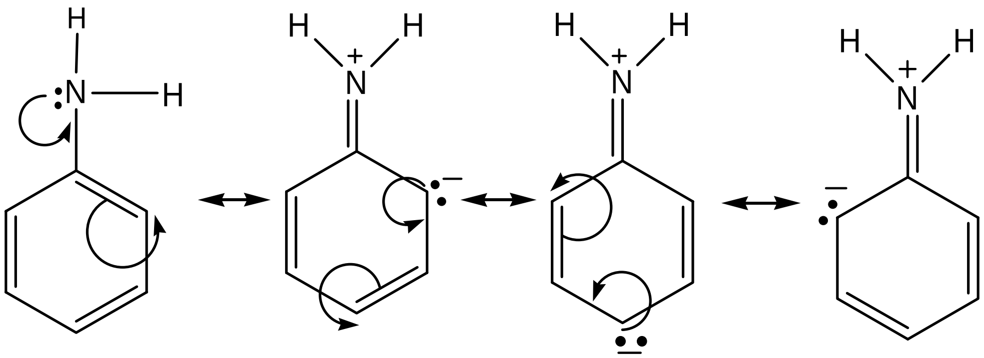


Figure 3.3 Reduced basicity of aniline due to electron pair delocalization

In pyridine nitrogen is sp^2 hybridized and non-bonding electron pair is localized on nitrogen atom. But increasing s-character brings it closer to nitrogen nucleus reducing its tendency to bond to a proton. The reduced basicity of para-nitroaniline is due to the presence of electron withdrawing group (NO_2). Presence of electron withdrawing groups such as CN or NO_2 in para- and ortho- positions in an amine group has large effect on the basicity of the compound. Benzylamine is relatively strong base compared to other aromatic amines due to the fact that electron pair is localized on nitrogen atom and it is sp^3 hybridized.

Table 3.2 pK_a values of simple aromatic amines in aqueous solutions at 25^oC and 1 Atm [9]

Compound	**pK_a**
Benzylamine	9.40 ± 0.20
Pyridine	5.32 ± 0.20
Aniline (phenylamine)	4.61 ± 0.20
Di-phenylamine	0.78 ± 0.20
Para-nitroaniline	1.01 ± 0.20

The increasing order of basicity in alkyl-amines is primary (1^o) > secondary (2^o) > tertiary (3^o) and when aromatic amines are compared to alkyl-amines, alkyl-amines are stronger bases than aromatic amines [7].

Volatility of amines

A variety of neutralizing amines is used in boiler and steam condensate systems for pH stabilization [10-18]. When added to feed water, a neutralizing amine must volatilize into steam for thorough distribution through out the system. The degree of volatilization of amine in such systems is measured by a quantity called distribution factor or distribution ratio (DR). Distribution ratio is defined as the ratio of amount of amine in vapor phase to the amount of amine in water phase (condensate) at a defined pressure or temperature. Amines with distribution ratio greater than 1.0 have more amine in vapor phase than the water phase.

$$\textit{Distribution Ratio} = \frac{\textit{Amount of amine in vapor phase (steam)}}{\textit{Amount of amine in liquid water (condensate)}}$$

Distribution ratios for commonly used neutralizing amines (at 1 atm) are tabulated in Table 2.3. As the distribution ratio is a function of temperature and pressure at any point in boiler / condensate system, the varying distribution ratios of commonly used NA amines affect their ability as neutralizing agents in certain locations where the amine is anticipated to be most effective.

Table 3.3 Distribution ratios of commonly used industrial amines.

Compound	**DR** [Ref. 17]	**pK$_a$ (25 ^{o}C, 1 atm)** [Ref. 8]	**Boiling Point (^{o}C)** [Ref. 8]
Morpholine	0.4	8.97 ± 0.20	128.9
Diethyl-aminoethanol	1.7	9.79±0.20	164
Dimethyl-isopropanolamine	1.7	9.43 ± 0.20	124.0
Cyclohexylamine	4.0	10.57 ± 0.20	134.5
Dimethylamine	3.0	10.73 ± 0.20	6.1 ± 3.0

Typical neutralizing amines have DR’s from 0.1 to 10; carbon dioxide has a DR of 100 or more depending upon temperature. Because of this difference in distribution ratios, amines and carbon dioxide tend to concentrate at remote locations within in the hydrothermal system making it impossible for an amine to completely neutralize the carbonic acid formed due to dissolved carbon dioxide.

The importance of distribution ratio of neutralizing amine in supercritical water is not yet quantified. Before addressing its importance, the stability of amines at extreme temperatures and pressures has to be evaluated. Once it is known that a particular amine is stable at such operating conditions, the influence of distribution ratio on its pH neutralizing capability can then be considered.

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CHAPTER IV

KINETICS AND MECHANISMS

The selection criterion for an amine as a pH stabilizing agent depends on its stability, basicity and volatility. If an amine is not stable in a solvent (in this case, water) at process operating temperatures and pressures, it decomposes forming undesirable light molecular weight compounds such as ammonia. Before evaluating amine basicity and volatility, it is important to figure out how stable the amine is. Different amines decompose in respective solvents at different rates based on their chemical structure, reactivity and process operating conditions.

Little data are available on decomposition kinetics of amines in supercritical water. This chapter focuses on two major topics, reaction kinetics and mechanisms which are fundamental in evaluating organic amine stability in supercritical water. Reaction kinetics of amines in this study is the decomposition or degradation kinetics; the reactants being the organic amine and water at supercritical conditions (T_c = 374 ^oC and P_c = 22.4 MPa). The usual way of investigating a chemical reaction is to start from stoichiometry, then the Kinetics, followed by investigation of the chemical mechanism involved. Stoichiometry of a reaction can be determined only when complete information of the final reaction products is known. The importance of stoichiometry will be discussed only when needed.

Literature Review

No literature was found investigating the degradation kinetics of amines in supercritical water highlighting their potential as pH stabilizing agents. Research involving supercritical water has focused on two broad areas until the mid 1900's; supercritical fluid extraction (SFE) and supercritical water oxidation (SCWO) [1, 2]. The Nuclear Energy Research Initiative (NERI) program (1999) initiated advanced research in promoting supercritical water as nuclear reactor coolant for power generation. The literature reviewed in this section is related to either supercritical fluid extraction (SFE) or supercritical water oxidation (SCWO). It is beyond the scope of this work to present extensive details about SFE or SCWO; the end uses of presented data in these sources may be for different purposes but it can help evaluate current research interests. The following sections are subcategorized based on compounds of similar structure and/or attached organic/inorganic molecular group.

Benzylamine

Houser and coworkers studied the reactions of 1,2,3,4-tetrahydroquinoline (THQ) and benzylamine in supercritical water [3]. These reactions were carried out in a batch reactor in presence of zinc chloride catalyst. Gaseous phase products were not analyzed after the completion of reaction; aqueous phase products were analyzed using standard gas chromatography and mass spectroscopy. It was observed that the rate of conversion of THQ is not influenced by the presence of $ZnCl_2$ catalyst. However, it did influence the formation of quinoline, a major product formed in the reaction, enhancing its yield. It was also reported that the presence of catalyst favors the formation of low molecular products such as ammonia. Only trace amounts of ammonia were found when the catalyst was not used.

Table 4.1 Products of benzylamine pyrolysis [Houser *et al.*, Ref. 3]

Time: 1h; Temperature: 400^{o}C; 100% reacted

Volatile products	**% yield**
Toluene	26.9
Benzonitrile	9.5
Diphenyl methane	1.2
Bibenzyl	18.1
Stilbene	11.7
Methylcarbazole	0.6
Diphenylmethylene indole	7
Triphenylimidazole	3.8
Tetraphenylpyrrole	6

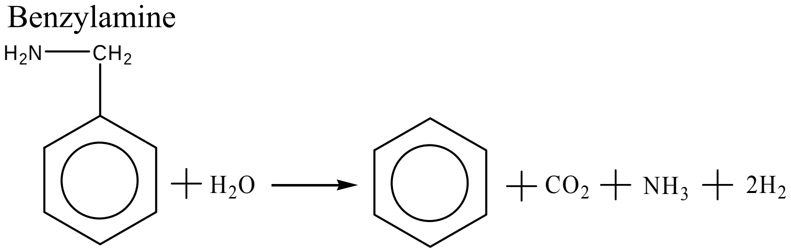
Experiments with benzylamine were carried out without $ZnCl_2$ catalyst. The final reaction products of pyrolysis were compared to reaction products of benzylamine and supercritical water reaction. Benzylamine completely reacted with supercritical water and it was reported that supercritical water has significant effect on the final reaction products.

Table 4.2 Reaction products of benzylamine in supercritical water [Houser *et al.*, Ref. 3]

Temperature [^oC]	400	450
H_2O pressure [MPa]	26.7	35.85
Time [h]	1	1
Volatile products	**% yield**	**% yield**
Ammonia	66	101
Toluene	48	49
Benzene	11	17
Benzaldehyde	13.5	8.5
Benzonitrile	0.1	0.2
Benzyl alcohol	2.0	1.8
Biphenyl	1.0	2.6
Diphenyl methane	0.4	0.6
Phenyltoluene isomers	1.4	3.4
Bibenzyl	2.0	1.8
Benzylidenebenzylamine	9.5	5.4
Minor products (total)	0.6	0.8

Neat (pure) pyrolysis of benzylamine produced toluene as major product and when reacted with supercritical water, the major product was ammonia. These results clearly indicate that reaction pathway of benzylamine is significantly different in supercritical water compared to neat pyrolysis. Reaction products of benzylamine with pyrolysis and supercritical water are tabulated in Tables 4.1 and 4.2.

Observation of Table 4.1 and 4.2 indicates that benzene, biphenyl and benzylidenebenzylamine (BBA) are absent in pyrolysis where as toluene, diphenyl methane and bibenzyl were common reaction products in both the reactions. This suggests that there might be two different reaction pathways for benzylamine decomposition in supercritical water. One pathway involves the formation of ammonia and toluene and the other involves the oxidation of benzylic carbon which results in formation of benzene. The latter pathway is possible only when there is a source of hydrogen present, in this case water. However, it has to be noted that ammonia is formed in trace quantities in pyrolysis. No kinetic data for the decomposition of benzylamine in supercritical water or pyrolysis have been reported. The possibility of two reaction mechanisms in supercritical water is qualitatively discussed but not confirmed. The second reaction pathway (oxidation/hydrolysis), where hydrogen is utilized, is



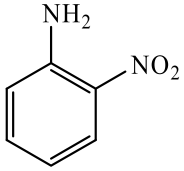
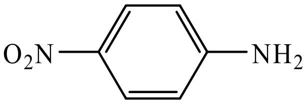
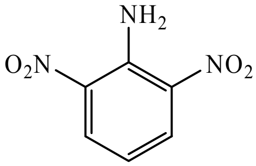
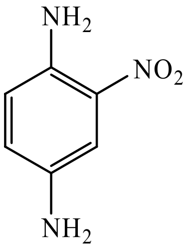
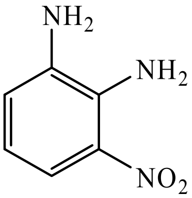
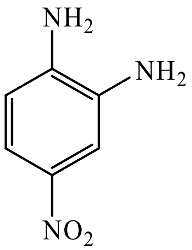
Nitro-anilines

Wang and coworkers studied the pyrolysis reaction pathways and stability of nitroanilines with nitro and amino substituents in high temperature water (100°C < T < 374°C) [4]. The compounds selected for this study are 2-nitroaniline (2NA), 4-nitroaniline (4NA), 2,6-dinitroaniline (2,6-DNA), 2-nitro-1,4-phenylenediamine (2NPDA), 3-nitro-1,2-phenylenediamine (3NPDA), and 4-nitro-1,2-phenylenediamine (4NPDA). All the experiments were carried out in batch reactors. It was reported that rates of decomposition of aromatic nitroamines were faster in high temperature water than for pyrolysis. It was also observed that there are two reaction pathways, hydrolysis and pyrolysis occurring in parallel in high-temperature water. These findings are in agreement with Houser *et al.* [3]. The pseudo first order rate constants for nitroanlines in high temperature water (T = 300 °C) were experimentally determined at reduced water density of $\rho_{r,w} = 0.518$. It was observed that rates of pyrolysis of di-substituted aromatic amines, 2NA and 4NA were similar and a significant increase in reaction rate was reported when a second amino (NH_2) group was added. Addition of second nitro group (NO_2) did not influence the pyrolysis rate significantly. It was reported that tri-substituted aromatic amines were more reactive than di-substituted ones. Further it was observed that tri-substituted nitroamines with multiple amino groups were more reactive than those with multiple nitro groups. Table 4.3 summarizes the pseudo-first order rate constants of nitroanilines. 2NPDA, 3NPDA and 4NPDA were observed to be thermally stable at $T \leq 200^{o}C$ (water density not reported) and all the three compounds reacted completely at $T = 300^{o}C$ ($\rho_{r,w} = 0.518$). Since all the experiments were carried out at fixed water density of $\rho_{r,w} = 0.518$, the influence of pressure (or water density) on the rate constant cannot be evaluated from presented data.

p-nitroaniline

Lee and coworkers investigated the reactivity of *para*-nitroaniline in supercritical water [5]. A tubular reactor was used to study the reaction under two different sets of conditions, reactivity in absence of oxygen (de-aerated water, hydrothermal decomposition/pyrolysis) and reactivity in presence of oxygen (oxidation/hydrolysis).

Table 4.3 Pseudo-first order rate constants of nitroanilines at T = 300°C
[Wang *et al.*, Ref. 4]

Reactant	Abbr	Initial concentration, C_o (mol L^{-1})	k x 10^3 (min^{-1})	
			$\rho_{r,w} = 0.0$	$\rho_{r,w} = 0.518$
	2NA	0.302	4.81 ± 0.71	20.72 ± 1.15
	4NA	0.302	4.88 ± 0.52	31.08 ± 5.46
	2,6-DNA	0.228	8.19 ± 0.39	67.48 ± 9.76
	2NPDA	0.272	358.52 ± 36.69	---
	3NPDA	0.272	254.92 ± 40.16	297.87 ± 33.69
	4NPDA	0.272	---	---

It was reported that overall reaction rate significantly increased with addition of oxygen. Activation energies of pyrolysis and pyrolysis combined with hydrolysis were calculated experimentally. The observed trends in the reaction rates are in agreement with data published by Wang *et al.* [4]. However, the authors did not address the key issues such as possible reaction mechanism and the effect of solvent density on the overall reaction rate which makes the kinetic model a mere correlation of generated experimental data and does not account for possible influence of solvent properties.

Benzylphenylamine

Abraham and Klein studied the pyrolysis reaction of benzyl phenyl amine (BPA) in sub and supercritical water [6]. All the reactions were carried out in a batch reactor at 340^{o}C (subcritical) and 386^{o}C (supercritical). The operating pressure at supercritical conditions was reported as $P_r = 1.09$ (reduced pressure). The major reaction products identified in both cases were aniline, benzyl alcohol and toluene, aniline being major product at sub and supercritical conditions. The yields of benzyl alcohol and toluene changed significantly with increase in reaction temperature, the former being the second major product to aniline at subcritical conditions and the latter being the second major product at supercritical conditions. It was observed that the reactivity of BPA was lower in supercritical water. The pseudo-first order rate constant for BPA reaction in subcritical water was observed to be 2.8×10^{-4} s^{-1} and in supercritical water the rate was 6.60×10^{-4} s^{-1}. The yields of major reaction products are summarized in Figures 4.1 and 4.2.

Townsend and coworkers studied chemical kinetics and reaction mechanisms of heteroatom containing coal model hydrocarbons in supercritical water [7]. One of the compounds investigated was benzylphenylamine at water densities of $0 < \rho_{r,w} < 2.1$ and T

= 386 ^oC. The major products observed were toluene, aniline and benzaniline at $\rho_{r,w}$ = 0.0 and benzyl alcohol at $\rho_{r,w}$ = 1.2. It was also observed that selectivity of aniline, was relatively uneffected by solvent density. However, solvent density was observed to significantly effect the selectivity of toluene which decreased as the water density increased indicating that pyrolysis is inhibited by increasing water density. The selectivity of benzyl alcohol was observed to increase with increasing water density indicating that increasing density favors hydrolysis. On the whole, decomposition of BPA in supercritical water is aided by parallel hydrolysis and pyrolysis pathways, hydrolysis dominating at high solvent densities and pyrolysis dominating at low densities. The conversion rates of BPA in pyrolysis ($\rho_{r,w}$ = 0.0) were observed to be higher (about 0.8) when compared to hydrolysis ($\rho_{r,w}$ = 1.2) where the conversion was around 0.7. These findings are not in agreement with the conversion rates observed by Wang *et al.* [5] for nitroanilines where the reaction rate rapidly increased with addition of water (T = 300 ^oC). It has to be noted that there is a difference in operating temperature of the experiments. Pyrolysis and hydrolysis products of BPA are summarized in Table 4.4. In addition to BPA, the authors also studied the reactions of dibenzyl ether, phenethyl phenyl ether, guaiacol, and benzyl phenyl ether. Based on the reaction products of these compounds in supercritical water and their pyrolysis products, it was concluded that the mechanism of hydrolysis in supercritical water requires a heteroatom (in case of BPA, nitrogen). Further, for hydrolysis mechanism to occur, the reactant (organic compound) should contain a saturated carbon to which the heteroatom is attached.

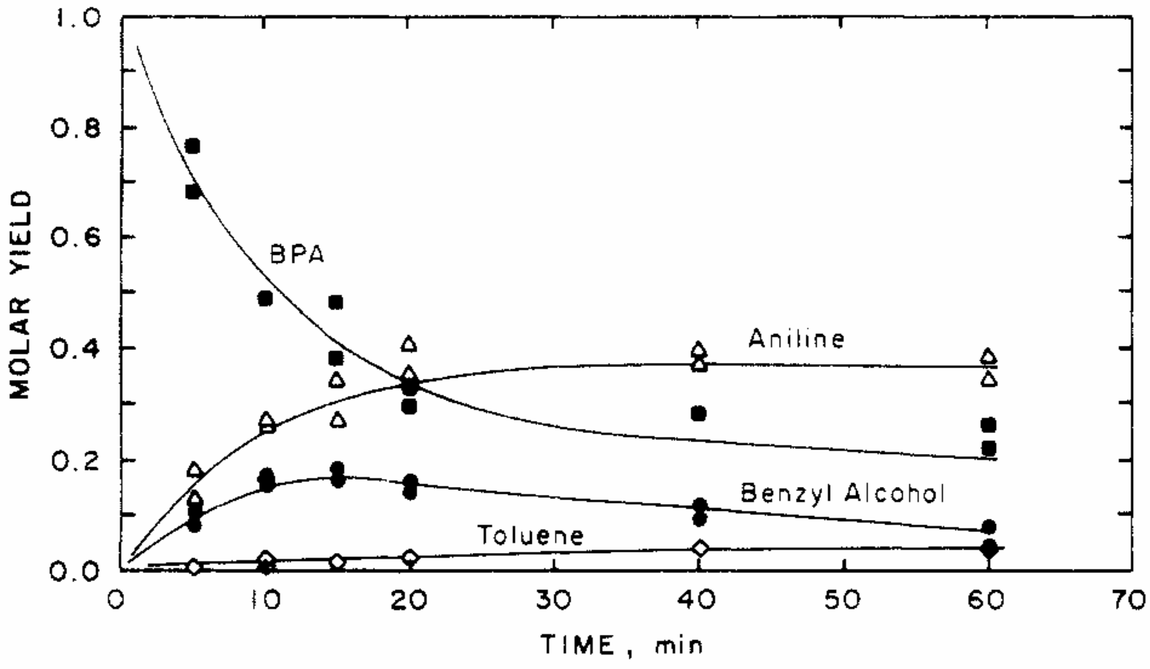


Figure 4.1 Yields of major reaction products of benzyl phenyl amine pyrolysis in water at 340°C [Abraham and Klein, Ref. 6]

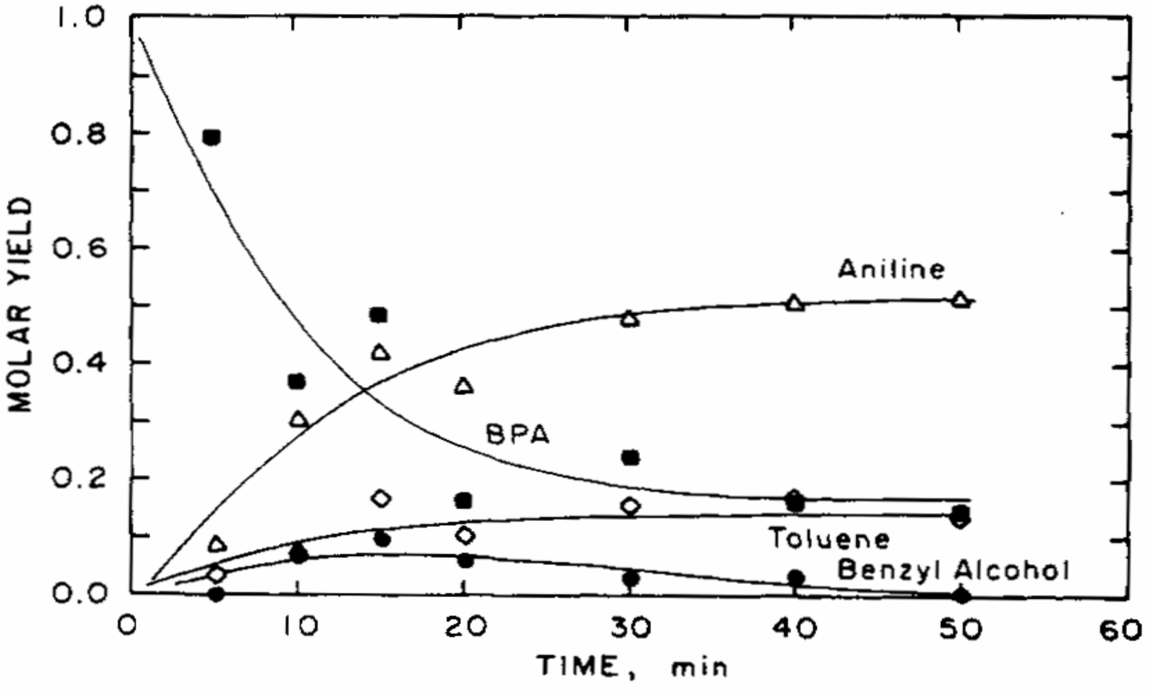
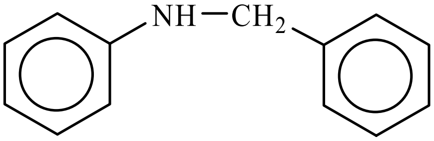
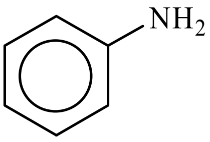
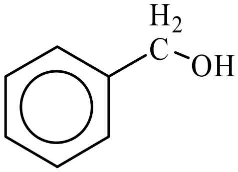
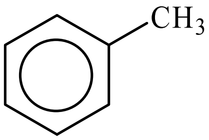
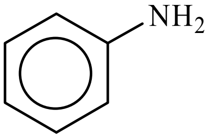


Figure 4.2 yields of major reaction products of benzyl phenyl amine pyrolysis in water at 386°C [Abraham and Klein, Ref. 6]

Table 4.4 Pyrolysis and hydrolysis products of benzyl phenyl amine at 386 °C
[Tounsend *et al.,* Ref. 7]

Reactant	Products	
	Pyrolysis $\rho_{r,w} = 0.0$	Hydrolysis $\rho_{r,w} = 1.2$
 Benzyl Phenyl Amine	 Aniline	 Benzyl Alcohol
	 Toluene	 Aniline

This mechanism is similar to nucleophilic attack of solvent on saturated carbon (Figure 4.3). Based on the reaction products of compounds examined, the authors suggested that the solvent di-electric constant may have a significant effect on the reaction rate. In order to evaluate this effect, kinetic data at varying solvent densities (thus varying di-electronic constant) have to be generated.

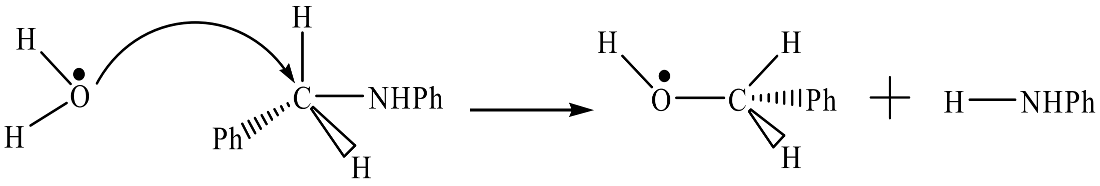


Figure 4.3 Nucleophilic attack of water on saturated carbon atom

Methylamine

Benjamin and Savage studied the reactions of methylamine in supercritical water from 386 and 500 °C and water densities from 40 to 540 kg m^{-3} [8]. Experiments were carried out in stainless-steel batch reactors; gas phase products were not analyzed. At low water densities ($\rho_w \leq 260$ kg m^{-3}) it was observed that reactivity of methylamine was not influenced by variation in solvent density and methylamine conversion was too low, the major reaction product was ammonia. In this low density region the conversion of methylamine almost remained constant. When the water density was increased above 260 kg m^{-3}, the reactivity of methylamine increased, and the major product formed in this high density region was methanol. Based on these observations, it was reported that pyrolysis of methylamine occurred in low water density region and hydrolysis dominated in high water density region. These findings are in agreement with results published by Houser *et al.* [3], Townsend *et al.* [7], and Wang *et al.* [4]. The experimental data at different temperatures were used to generate Arrhenius relation for rate constant in low density region (ρ_w less than 300 kg m^{-3}) where solvent has barely any effect over the reaction kinetics.

The proposed Arrhenius equation is

$$k = 10^{6.1 \pm 2.0} \exp\left(\frac{-38 \pm 7 kcal/mol}{RT} \right), (mol/cm^3)^{0.34} s^{-1}$$

The order of reaction with respect of methylamine in this region was found to be 0.66 ± 0.11 which further gives the global rate expression of methylamine degradation kinetics in supercritical water at water densities below 300 kg m^{-3} as

$$-r_{CH_3NH_2} = 10^{6.1\pm2.0}\exp\left(\frac{-38\pm7kcal/mol}{RT}\right)\times[CH_3NH_2]^{0.66\pm0.11}$$

This rate expression can be used only when solvent (water) is not anticipated to participate in the reaction i.e., in low density region. The possible mechanism for methylamine degradation is unknown at this point. The major reaction product formed in high water density region ($\rho_w > 260$ kg m^{-3}) was methanol aided by hydrolysis. Kinetic data of methylamine reactivity in hydrolysis was used to calculate reaction order with respect to water. The proposed expression is as follows

$$Y_{CH_3OH} = 1-\exp(-10^{-1.7\pm0.6}[H_2O]^{2.0\pm0.4}t)$$

where Y_{CH_3OH}, molar yield of methanol and *t* is the time. Note that this expression is a correlation of kinetic data and does not incorporate the effects of solvent such as density or any other property which has potential to alter the reaction kinetics.

Possible Mechanisms

To summarize the literature reviewed in previous section, the possible mechanisms by which amines decompose in supercritical water include ionic and free radical mechanisms [4, 6, 8]. The properties of supercritical water may enhance or inhibit the reaction to proceed through these mechanisms depending on the operating conditions. For example at extremely low water densities, water molecules barely participate in the reaction. In such case, it can be assumed that the amine undergoes thermal decomposition and free radical chemistry can be used to interpret the reaction kinetics from products formed.

Free radical mechanism

Higashihara and coworkers studied the thermal decomposition of methylamine in the temperature range of 1400 and 1820 K [9]. The possible steps involved in the decomposition according to them is

$$CH_3NH_2 \longrightarrow CH_3 + NH_2$$

$$CH_3 + CH_3NH_2 \longrightarrow CH_4 + CH_2NH_2$$

$$CH_3 + CH_2NH_2 \longrightarrow CH_4 + CH_2NH$$

$$NH_2 + CH_3NH_2 \longrightarrow NH_3 + CH_2NH_2$$

$$NH_2 + CH_2NH_2 \longrightarrow NH_3 + CH_2NH$$

$$CH_2NH \longrightarrow H_2 + HCN$$

With increase in water density, the concentration of hydroxyl and hydronium ions increase resulting in the increased possibility for water to participate in the reaction. This might significantly change products formed in the reaction steps shown above. Hence free radical chemistry can be used to explain the product formation in low water density region where pyrolysis is major reaction pathway. If water is assumed to participate in the reaction at elevated water densities then the reaction pathway can be interpreted through either ionic or molecular mechanisms.

Ionic mechanism

Most of the reactions involving organic compounds through ionic pathway include substitution reactions on carbon atom [10]. In case of organic amines in supercritical water, there is a possibility for the reaction to occur through nucleophilic substitution reaction, the nucleophile, X being either hydroxyl ion or water molecule itself (Figure 4.4). The nucleophilic substitutions reactions fall into two categories, S_N1 and S_N2 [11]. S_N1 stands for substitution nucleophilic uni-molecular and S_N2 stands for substitution nucleophilic bi-molecular. In S_N1 reaction, the global reaction rate is independent of concentration of nucleophile where as in S_N2 reaction global reaction rate is dependent on the concentrations of both amine and attacking nucleophile.

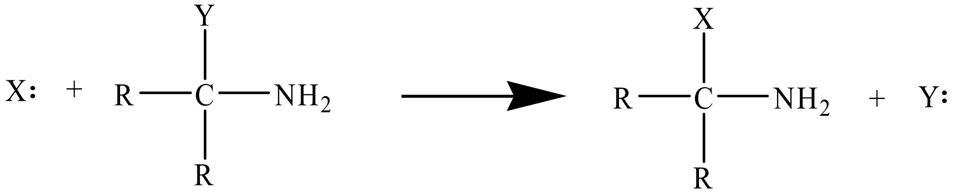


Figure 4.4 Substitution reactions of amines

The qualitative picture of these two reactions is that in S_N2 mechanism the nucleophile attacks the amine molecule forcing it to depart (Figure 4.5) where as S_N1 mechanism proceeds through the stabilization transition complex by the cation formed from amine molecule followed by subsequent attack of nucleophile on cation. The structure of amine molecule plays an important role in determining whether the substitution is carried through S_N1 or S_N2 mechanisms. For example, S_N2 mechanism is likely to operate if the substitution site is sterically unhindered (Figure 4.5). The nucleophilic substitution mechanism is likely to occur only when water molecules actively participate in the reaction.

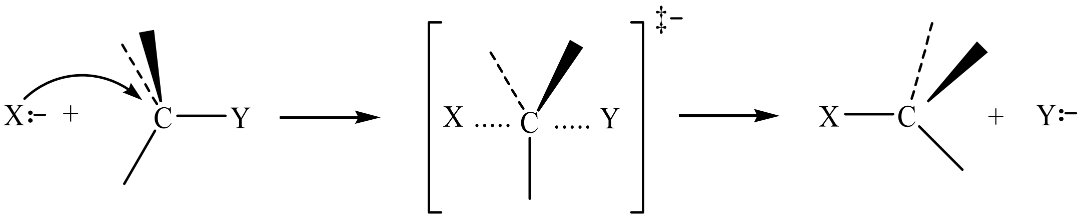


Figure 4.5 Transition state complex in S_N2 reaction

The reaction kinetics alone is not sufficient to distinguish between S_N1 and S_N2 mechanism pathways in a solution [10]. This is because in any solution as the reaction proceeds, the concentration of solvent nucleophile participating in the reaction is always in excess and does not change significantly. S_N2 mechanism consists of a single elementary step in which nucleophile attacks the amine to form final product where as S_N1 mechanism consists of two steps: rate determining step of amine dissociation to carbocation and subsequent rapid attack of nucleophile on carbocation. So the possibility of a bimolecular reaction cannot be ruled out when the reaction rate is independent of nucleophile concentration.

Discussion

To summarize the results in this section, organic amines decompose in supercritical water aided by pyrolysis at low water density and by both pyrolysis and hydrolysis at high density; the density of water at which a shift from pyrolysis to hydrolysis takes place is compound specific. Taking into account the fact that supercritical water supports free radical, polar and ionic mechanisms [11], the literature on organic amine degradation mechanisms in supercritical water is sparse. Careful observation of published kinetic data of methylamine reveals that methylamine is more stable than benzyl phenyl amine (BPA) and benzylamine (BA) in water at supercritical conditions. This behavior can be attributed to weaker C-N bonds in aromatic compounds [8]. From these investigations it can be taken for granted that aliphatic amines are more stable than aromatic amines in supercritical water and can serve as good pH neutralizing agents.

The influence of solvent properties is dominant on reaction kinetics, especially in hydrolysis [6-8, 11]. Better prediction of conversion rates is possible if these solvent effects are taken into consideration while formulating the rate equation. Such solvent effects include the effect of dielectric constant of water (ε) [4, 7, 8, 12-20], density of water (ρ_w) and ionic product of water (K_w) [21]. When searching for the possible reaction mechanism, it should be noted that mechanism and kinetic equation are interdependent. Hence the approach for determination of reaction mechanism is an iterative process in which certain changes in kinetic rate equation should to be made.

The stability of methylamine in supercritical water gave hope that amines have the potential to remain stable and neutralize the acid concentration. The effect of supercritical state of water on reactivity of amines has to be addressed next. The next chapter deals with possible interaction of solvent and the effects of its properties on reaction rate of amine in supercritical water and on their basicity.

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CHAPTER V

SOLVENT EFFECTS

Water, when heated from ambient to supercritical conditions, transforms from being a dense, strongly-polar, hydrogen-bonded liquid to a lower density, non-polar fluid with gas like diffusivity and viscosity [1-3]. Supercritical water exhibits properties that are very different from those of ambient liquid water. Supercritical water has a lower dielectric constant, fewer and weaker hydrogen bonds and a high isothermal compressibility than ambient liquid water. The ion product, or dissociation constant (K_W) for water as it approaches the critical point, is about 3 orders of magnitude than it is for ambient liquid water. Beyond the critical point K_W decreases dramatically making supercritical water a poor medium for ionic chemistry. For example K_W is about nine orders of magnitude lower at 600 °C and about 24 MPa than it is at ambient conditions.

The literature available on reactions of various organic compounds including amines in supercritical water provides strong precedent for noticeable solvent effects on reaction rates. The quantities most likely to affect reaction rate of amines and other organic compounds in supercritical water are density and dielectric nature of the solvent. The possible reaction mechanisms involved in the degradation of organic amines in supercritical water involves free-radical, ionic and molecular mechanisms. The free-radical mechanism is predominantly observed in low-water density region where the reaction pathway proceeds through pyrolysis of amine molecule. It is in the hydrolysis region where there is a possibility of amine undergoing degradation through ionic and molecular mechanisms [6]. The affect of properties of solvent medium on these reaction pathways in hydrolysis contributes to the deviation of reaction rate from Arrhenius-like behavior.

Literature Review

Townsend *et al*. [4] observed parallel pyrolysis and hydrolysis reaction mechanisms of coal model compounds in supercritical water and it was reported that hydrolysis reaction rate of dibenzylether and guaiocol is strongly dependent on the dielectric constant of the solvent medium. Similar trends were observed in the study of reactions of nitroaniline explosive simulants in high temperature and supercritical water by Wang *et al.* [5]. Benjamin and Savage [6] studied the reaction of methylamine in supercritical water and found that solvent dielectric constant has significant effect on the reaction rate. In addition, they reported that hydrolysis mechanism may be aided either by S_N2 or molecular mechanism with one water molecule in which the transition state is more polar than the reactants. A dielectric constant dependent term was incorporated by Iyer and Klein [7] into the rate equation for correlating the rate constant of butyronitrile hydrolysis to account for changes in the electrostatic nature of solvent resulting from pressure variation. Improved fits in the reaction model of synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol in liquid ethanol were observed by Habenicht *et al*. [8] when the influence of solvent dielectric constant was taken into account. Xiang and Johnston [9] studied the reaction of β-naphthol and base (OH^-) in supercritical water up to 400^oC and 470 bar and reported that density and dielectric nature of solvent influences the equilibrium rate constant at constant temperature. Ryan *et al.* [10] investigated the dynamics of proton transfer from 2-naphthol to various bases in sub and supercritical water and reported that dielectric constant of reaction medium has significant effect on the proton transfer reaction. González and Montané [11] observed that the reaction rate of Dibenzylether hydrolysis in supercritical water is lowered with increase in dielectric constant of solvent medium indicating that transition complex is less polar than the reactants. Venardou *et al.* [12] investigated the hydrolysis reaction of acetonitrile at near critical conditions and suggested that solvent properties like dielectric constant and ionic product may have a significant affect on the reaction rate and final product composition. Researchers at Massachusetts Institute of Technology incorporated a correction term into their rate expression which accounts for solvation effects in the reaction kinetics of methylene chloride in sub and supercritical conditions [13-14].

Ion Product (K_W)

Literature concerning hydrolysis of organic amines in near critical and supercritical water suggests that there is a possibility for reaction pathway to proceed through ionic mechanism. Three such possible mechanisms in hydrolysis region were suggested by Benjamin and Savage [6]:

1. S_N2 reaction with water as nucleophile
2. S_N2 reaction with hydroxyl ion as nucleophile (base-catalyzed)
3. Protonation of organic amine by hydronium ion (acid-catalyzed)

These mechanisms were discussed in detail in Chapter IV. All the above mechanisms involve either hydroxyl ion (OH^-) or hydronium ion (H_3O^+), or both. The concentration of hydroxyl and hydronium ions (or concentration of water) is expressed by ion product (K_W) of water at specific temperature and pressure. K_W of water is not a strong function of pressure at sub-critical conditions. However, beyond the critical point, it varies dramatically with increase in pressure (Figure 5.1). Ion product when plotted against density, a smooth curve is observed (Figure 5.2). If the reaction pathway follows ionic mechanism, then very slight changes in pressure can dramatically change the ionic product further influencing the rate determining kinetic equation.

Now it is evident that ion product of water is a key parameter for tuning the reaction rate in hydrolysis region provided the reaction pathway is through ionic mechanism. The next step is to evaluate the conditions favorable for reaction to proceed through ionic pathway. Ionic mechanisms in any aqueous system are favored when $K_W > 10^{-14}$ [15]. At such relatively higher concentration of hydroxyl and hydronium ions, the probability of attack by one of either ion on amine molecule in amine – water system is higher. From Figure 5.2, it can be inferred that increase in pressure increases the ion product of water at a fixed density. Although the variation in ion product with pressure at a fixed density is low, this behavior can help fine tune ion product to desired values with variation in pressure. At conditions where $K_W << 10^{-14}$ (Figure 5.2), the concentration of hydroxyl and hydronium ions in water is lowered resulting in low probability for ionic mechanisms. In this region, radical mechanisms dominate are most favored in systems with water as a solvent medium.

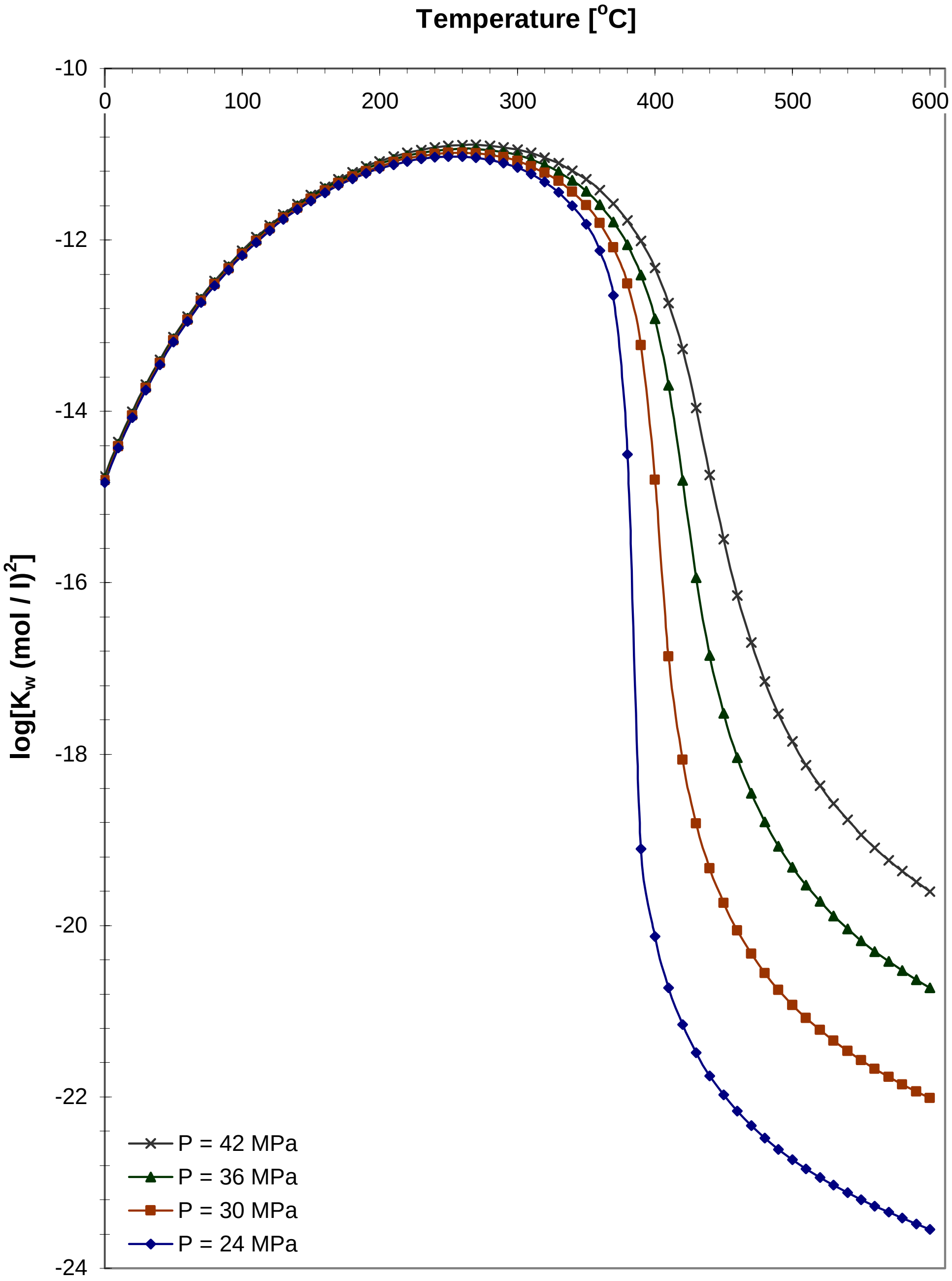

Figure 5.1 Isobaric variation of Ion Product of water (K_W) with temperature [19]

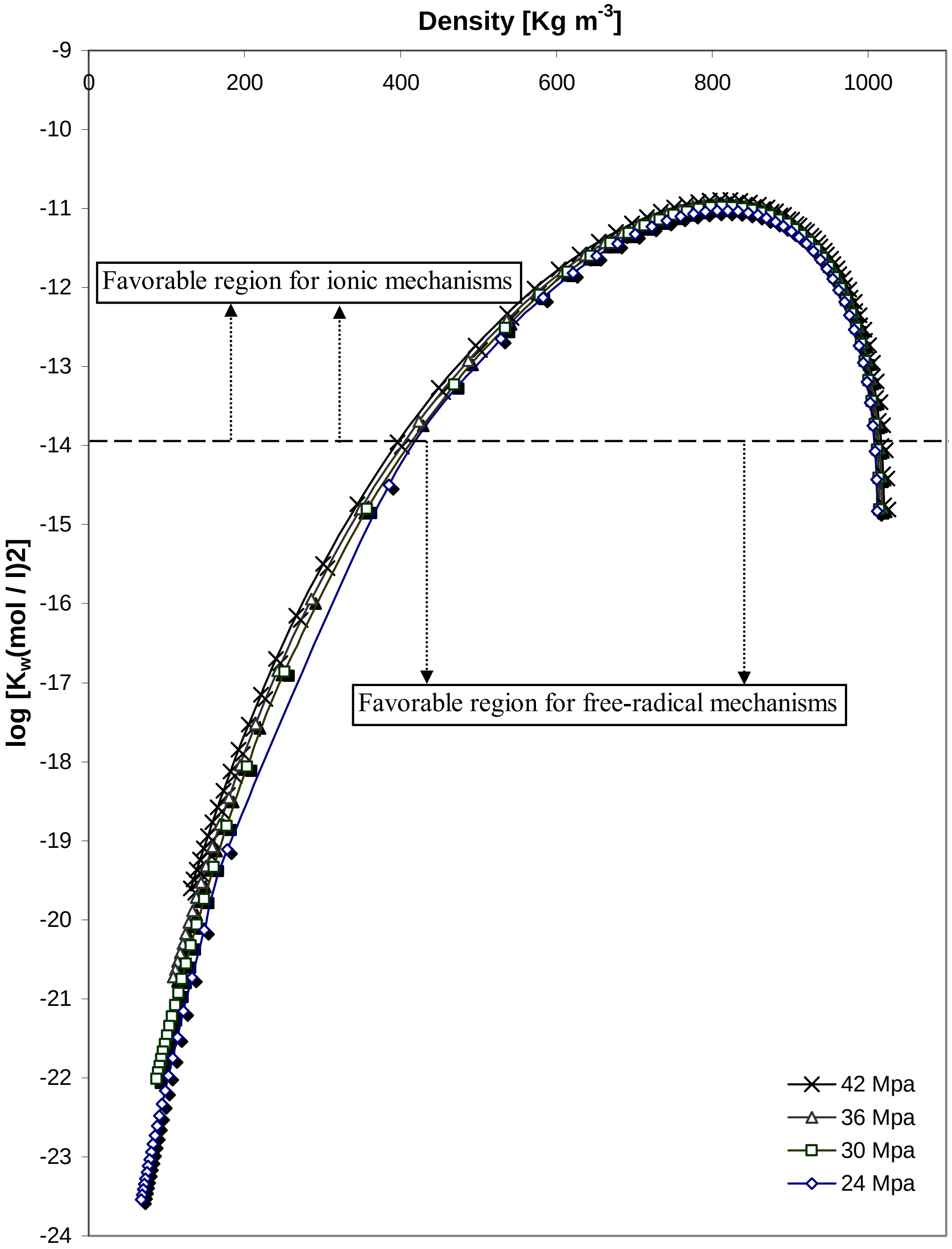

Figure 5.2 Isobaric variation of Ion product of water (K_W) with density [19]

Dielectric constant (ε)

Previous studies [4, 6] showed that hydrolysis of organic compounds in supercritical water can be interpreted using transition state theory. According to transition state theory, the rate constant for reaction at temperature T and density ρ is given by

$$k = \kappa\left[\frac{k_B T}{h}\right]\rho^{(1-n)} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{5.1}$$

where

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger} \tag{5.2}$$

Where κ is the transmission coefficient, n is the sum of reactants stoichiometric coefficients, and $\Delta G^{\ddagger}$ is the free energy of activation [16]. For the reaction occurring in solvent medium, the solute (organic amine) – solvent (water) interactions influence the rate constant by modifying the free energy of activation and transmission coefficient. The change in free energy of activation due to solvent-solute interactions are termed as equilibrium solvation effects. In such cases, the pressure and density dependence of reaction rate can be derived from equations 5.1 and 2.

$$\left[\frac{\partial \ln k}{\partial P}\right]_T = (1-n)\kappa_T - \frac{\Delta v^{\ddagger}}{\mathrm{RT}} \tag{5.3}$$

$$\left[\frac{\partial \ln k}{\partial \rho}\right]_T = \frac{1-n}{\rho} - \frac{1}{\rho\kappa_T}\left(\frac{\Delta v^{\ddagger}}{\mathrm{RT}}\right) \tag{5.4}$$

Where κ_T is isothermal compressibility and $\Delta v^{\ddagger}$ is activation volume given by

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5.5}$$

and

$$\Delta v^{\ddagger} = -RT\left(\frac{\partial \ln K^{\ddagger}}{\partial P}\right)_T \tag{5.6}$$

The activation volume is the difference between the partial molar volumes of the transition state and the reactants and is strongly dependent on solute-solvent interactions. The effect of temperature, pressure and density on the solvation of reactants and transition state species in supercritical water may significantly change the kinetics of organic amine reaction as indicated by equations 5.3 and 4. The effect of these parameters may change depending on the characteristics of transition state. For example, if the transition state involves reactants with charge localization (ions) or polar molecules, then electrostatic interactions between the solvent and solute would influence the reaction kinetics. Dielectric constant of solvent in such instances may play a critical role in solvation of reactants and transition state species in water. The qualitative picture of solvent dielectric effect on reaction rate is that reactions involving a transition state more polar than individual reactants facilitate by increasing dielectric constant and reactions involving a transition state that is less polar than individual reactants are facilitated by decreasing dielectric constant.

The conventional approach of evaluating the effect of dielectric constant on reaction rate includes the use of Kirkwood theory [17-18]. For reactions involving changing dipole moment, Kirkwood theory quantifies the effect of solvent polarity on the reaction rate. Consider the following reaction of two polar molecules:

$$A + B \rightarrow X^{\ddagger} \rightarrow \text{Products} \tag{5.7}$$

According to Kirkwood theory, the rate constant of the above reaction is given by

$$\ln(k) = \ln(k_0) + \frac{N}{RT}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)\left[\frac{\mu_{X\ddagger}^2}{r_{X\ddagger}^3} + \frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3}\right] \tag{5.8}$$

where k_0 is the value of rate constant in reference state of unit activity coefficients, $X^{\ddagger}$ is transition state species, μ the dipole moment, r the molecular/complex radius, N Avogadro number, and ε the solvent dielectric constant. According to this theory, a plot of ln(k) vs $1/\varepsilon$ should be linear. The slope of the plot determines the relative polarity of transition state compared to the reactants. A positive plot of ln(k) vs $1/\varepsilon$ indicates that the reaction proceeds through a transition state less polar than the reactants and vice versa. Figure 5.3 shows the sample Kirkwood plot for kinetics of methylamine methylamine hydrolysis in supercritical water at 410 °C.

Other effects

The literature highlights dielectric constant and ion product of water as two major solvent effects which can alter the hydrolysis reaction rate of various organic compounds in supercritical water. However, effect of key variables like solvent structure and hydrogen bonding on reaction rate is unknown.

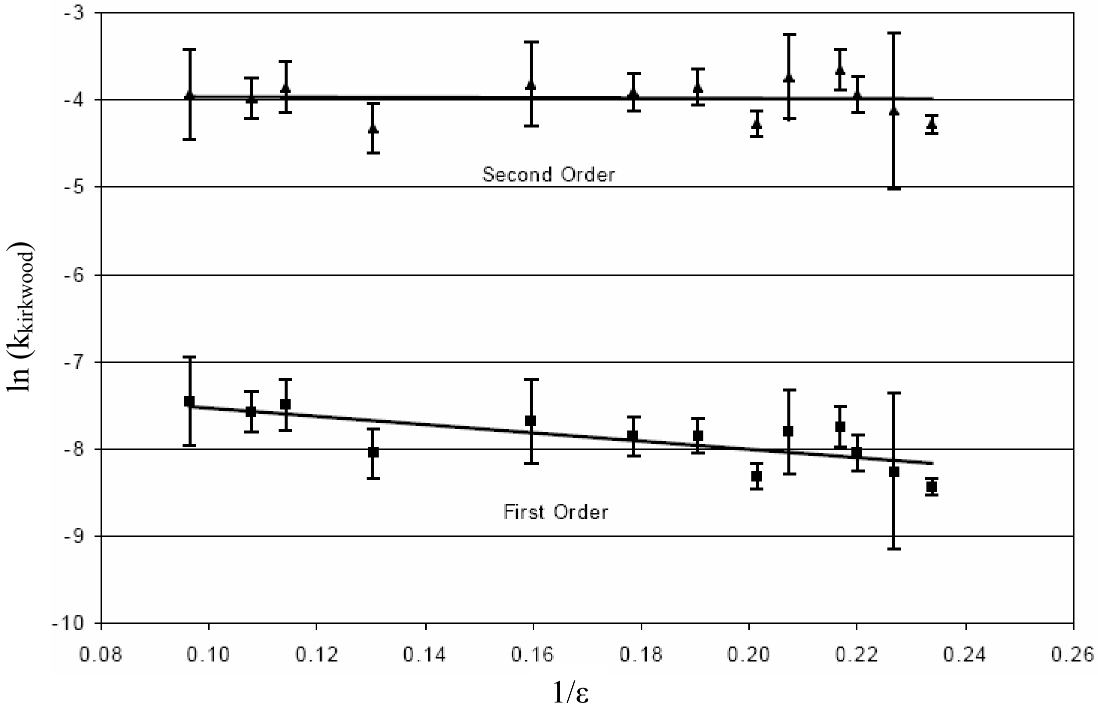

Figure 5.3 Kirkwood plot showing dependency of hydrolysis rate constant on dielectric constant of solvent – hydrolysis of methylamine in supercritical water at 410°C (Ref. 6.)

Modification of kinetic equation

Conventional kinetic analysis

Consider the following reaction between organic amine and water at ambient conditions. Although amines are relatively inert in ambient water, a hypothetical case is presented below.

$$\text{A (amine)} + \text{B (water)} \rightarrow \text{Product 1 (C)} + \text{Product 2 (D)} \tag{5.9}$$

The rate expression for the disappearance of A is given by

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \tag{5.10}$$

where *k* is the rate constant. According to Arrhenius expression form of rate constant, this would be

$$k = k_0 e^{-E/RT} \tag{5.11}$$

Where k_0 is the frequency factor and E is activation energy of the reaction. The concentration of water will not change appreciably during the course of reaction. Therefore the rate dependence on A can be isolated and can be written as

$$-r_A = -\frac{dC_A}{dt} = k' C_A^a \tag{5.12}$$

where *k'* is pseudo first order rate constant, given by

$$k' = \left(k.C_B^b\right) \tag{5.13}$$

Integrating equation 5.12 from time *0* to *t* seconds and C_{A0} to C_A, C_{A0} being the initial concentration, one would end up with the following equation:

$$\ln(t) = (1-a)\ln(C_{A0}) + \ln\frac{\left(F^{1-a}-1\right)}{k'(a-1)} \tag{5.14}$$

where F is fractional conversion, $F = {C_A}/{C_{A0}}$

Experimental data can then be generated at various initial concentrations (C_{A0}) and varying reaction times.

Temperature	Initial concentration of organic amine (C_{A0})	Time of reaction (t)	Final concentration of organic amine (C_A)
T_1	$(C_{A0})_1$	t_1	$(C_A)_1$
	$(C_{A0})_2$	t_2	$(C_A)_2$
	$(C_{A0})_3$	t_3	$(C_A)_3$
T_2	$(C_{A0})_1$	t_1	$(C_A)_1$
	$(C_{A0})_2$	t_2	$(C_A)_2$
	$(C_{A0})_3$	t_3	$(C_A)_3$

Table 5.1 Sample set of data points necessary to compute the rate constant and Arrhenius parameters of organic amine degradation

Once the experimental data is generated, equation 5.14 can be used to create a linear plot of ln(t) versus ln (C_{A0}), the slope of plot, *(1-a)* and intercept on ln(t) axis being $\ln \frac{\left(F^{1-a} - 1\right)}{k'\left(a - 1\right)}$. The slope of the, *(1-a)* is positive and greater than one, then the reaction has a negative order with respect to C_A. If the slope is positive and less than one, then the order of reaction is positive with respect to C_A. *k'* can be calculated from the intercept of plot on ln(t) axis and finally the global reaction rate constant, k can be computed using equation 5.13. To evaluate the activation energy and frequency factor of the reaction, similar set of experiments should be performed at a different temperature to generate Arrhenius plot [20].

The above presented conventional kinetic analysis would be sufficient to determine the rate kinetics of organic amines in supercritical water at very low water densities where the solvent effects are negligible. In this region, water is not an active participant in the reaction and decomposition of amines could be aided by cracking of molecular species. In other words, pyrolysis of organic molecules dominates in this region and use of conventional methods to correlate the kinetic data would be sufficient to obtain a fair approximation of rate constant. The threshold value of water density above which the solvent effects would alter the rate constant may be specific to the organic amine (or compound) participating in the reaction. Above this threshold value of density, water is an active participant in the reaction and may significantly change the overall stoichiometry of the reaction resulting in formation of new products. With continuous increase in water density, a transition from pyrolytic region to hydrolysis region takes places. During this transition, the two reaction pathways may proceed in parallel, with different rates with different product formations. Of these two reactions, the rate of hydrolysis (and probably pyrolysis too) reaction may be significantly altered by the changing physical properties of solvent (Dielectric constant, Ion product and Hydrogen bonding). Or it can be said that rate of reaction is a function of temperature, concentration of reactants and solvent properties.

$$-r_A = f(\text{temperature, concentration of reactants}, K_W, \varepsilon, \text{H-bonding}) \tag{5.15}$$

$$-r_A = \psi C_A^a C_B^b \tag{5.16}$$

where Ψ is new rate constant and is a function of temperature and solvent properties.

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CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The study reported in this thesis included (a) an extensive review of literature available on possible reaction pathways of organic amines in supercritical water and (b) possible solvent parameters that can affect the rate of reaction of organic amines in supercritical water.

Reaction pathways of amine degradation

1. Organic amines decompose in supercritical water through pyrolysis and / or hydrolysis pathways,
2. Pyrolysis is favored in low water density region (typically $\rho_w << 0.4$ kg m^{-3}) and hydrolysis pathway is favored in high water density region ($\rho_w > 0.4$ kg m^{-3}),
3. There is a possibility for the two reaction pathways to proceed in parallel with equal or unequal rates within a range of water densities, the range being specific to selected organic amine,
4. The available literature is not sufficient to generate a robust procedure to quantify the reaction rates of the two mechanisms,

5. The decomposition rate of amine through pyrolysis pathway in low water density region can be interpreted using free radical chemistry, and
6. The decomposition rate of amine through hydrolysis pathway in high water density region can be interpreted by nucleophilic substitution mechanisms.

Water effects in supercritical state

1. Pyrolysis of amine decomposition in low water density region is independent of properties of water
2. Rate of decomposition through hydrolysis is altered by dielectric constant and ion product of water at elevated water densities
3. The nature of dielectric constant influence on hydrolysis reaction can be evaluated using conventional Kirkwood analysis
4. The change in reaction pathway, either from pyrolysis to hydrolysis or hydrolysis to pyrolysis is accompanied by changes in water density and further, changes in ion product of water

To conclude, organic amines decompose in supercritical water and can serve as potential corrosion inhibitors when used in hydrothermal systems operating above critical point. Out of the three key parameters for selection an amine, stability, volatility and basicity, this report presented the results of investigation on the stability of amines by evaluating possible reaction mechanisms and kinetics. The volatility of amines which is an important factor to be considered when used in sub-critical systems may not have an impact in supercritical systems as the amine itself is in a supercritical state. Finally, no previous work was found evaluating the basicity of amines in supercritical water and significant amount of work should be done in this area to determine the acid - base behavior of amines in water beyond the critical point.

Recommendations

Literature available on reactions kinetics of organic amines in supercritical water is sparse. The kinetic data of amine reaction in supercritical water available till date include reactant conversions and product yields as functions of temperature and initial concentrations in batch reactors. None of the works reported analyzing the gas phase products formed after completion of reaction. These available experimental data are accompanied by a discussion of complementary mechanistic modeling components, not validated by experimental data.

There is a necessity to develop robust mechanistic and kinetic models to predict the elementary reaction rates and global kinetics of amine degradation in supercritical water. The model predictions should be compared with experimental measurements of intermediate molecular and free radical species of the reaction. Such measurements would need to be made in situ, and till date there have been no reports for measuring radical and molecular species concentrations during organic chemical reactions in supercritical water systems.

Experimentation

Experiments can be conducted either in batch or plug flow reactors. The reaction amine in supercritical state should be continuously monitored for any intermediate products formed. An ideal solution to monitor the reaction intermediates in situ would be use of spectroscopic techniques such as fiber-optic Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy and emission spectroscopy. The use of spectroscopic techniques would facilitate in examining the possible reaction intermediates in situ based on their respective wave characteristics. Temperature, pressure and pH in spectroscopic cell can be measured using conventional thermocouples, transducers and pH measurement devices. The sample can then be cooled to ambient temperature, vapor phase separated from liquid and analyzed for respective concentrations using Gas Chromatography (G.C) and Mass Spectroscopic (M.S) techniques. Notice that initial spectroscopic measurements are made in situ at supercritical conditions followed by G.C-M.S analysis at ambient temperature and pressure. This procedure would provide sufficient information on the reaction intermediate products and final reaction products in vapor as well as in liquid phases. It would also facilitate in investigation of acid – base behavior of organic amines in supercritical water and further investigation in molecular dynamics of solute – solvent interactions at supercritical conditions.

Rate equation

For accurate prediction of rate of decomposition of amines in supercritical water there is a necessity for development a global kinetic rate equation over a wide range of operating conditions. Considering the fact that the properties of supercritical water, density, ion product and dielectric constant are extremely sensitive to changes in temperature and pressure, and have the potential to alter the decomposition reaction pathway and reaction kinetics of amines, it is essential to incorporate these solvent effects into global kinetic equation.

An alternative approach to attain the goal is to breakdown the range of operating conditions based on density at which a shift of reaction pathway occurs. The reason for selecting density as a fundamental property here is that dielectric constant and ion product of water have smooth variation with density and can be easily correlated with the same.

Three possible regimes can be identified based on decomposition pathways:

I. $0 < \rho_w < \rho_{wPT}$ where ρ_w is water density and ρ_{wPT} is the value of density below which solvent effects can be neglected and reaction pathway is assumed to be aided by pyrolysis pathway only. In this region water is not an active participant in the reaction and major amount of organic amine can be assumed to decompose through thermal cracking

II. $\rho_{wTH} < \rho_w < \rho_{MOP}$ where ρ_{wTH} is the value of water density above which reaction pathway is assumed to proceed only through hydrolysis. Water is an active participant in the reaction in this region; ion product and dielectric constant of water have significant influence on reaction kinetics. In this region, major amount of organic amine is assumed to decompose through ionic mechanisms. ρ_{MOP} is water density at maximum operating pressure and minimum operating temperature

III. $\rho_{wPT} < \rho_w < \rho_{wTH}$. In this region, the decomposition of amine is aided by both hydrolysis and pyrolysis. This regime can be visualized as a transition region where amine is partially decomposed through thermal degradation and partially through reaction with water (hydrolysis). The reaction pathway in this region is a function of localized density due to formation and dissociation of clusters of water molecules. Amine decomposes through hydrolysis pathway only if amine molecule is located within a cluster of water molecules where the probability for water molecule to participate in the reaction is higher.

This methodology of breaking down the operating range based on density would result in three different rate equations for the three regimes discussed above. The three rate expressions would then be of the form

$$-r_I = f(Temperature, Concentration)\Pi_I \tag{6.1}$$

$$-r_{II} = f(Temperature, Concentration, \varepsilon, K_W)\Pi_{II} \tag{6.2}$$

$$-r_{III} = f(Temperature, Concentration, \varepsilon, K_W)\Pi_{III} \tag{6.3}$$

Where r_I, r_{II}, r_{III} are rates of decomposition of amine in region I, II and III. Note that rate in equation 6.1 is independent of solvent properties. Π_I in equation 6.1 is correction factor for rate equation that takes into account reaction with water, if any. Similarly Π_{II} in equation 6.2 is correction factor in region II to take into account the reaction purely by thermal degradation. In equation 6.3, Π_{III} should incorporate the effects of varying rates of two different reaction pathways, pyrolysis through free radical mechanism and hydrolysis through ionic mechanism.

Finally, little data on dissociation constants of amines in supercritical water are available in literature which limits this study to evaluate the basic strength of organic amines. Availability of such experimental data would also contribute in evaluating the multiple steps involved in ionic mechanisms in hydrolysis region.

APPENDIX A

THERMODYNAMIC DATA OF WATER:
SUB AND SUPERCRITICAL CONDITIONS

A-I. Dielectric Constant of Water

Dielectric constant of water is calculated from the following correlation proposed by Uematsu and Franck:

$$\begin{aligned}\varepsilon = 1 &+ \left(A_1 / T^*\right)\rho^* \\ &+ \left(A_2 / T^* + A_3 + A_4 T^*\right)\rho^{*2} \\ &+ \left(A_5 / T^* + A_6 T^* + A_7 T^{*2}\right)\rho^{*2} \\ &+ \left(A_8 / T^{*2} + A_9 / T^* + A_{10}\right)\rho^{*4}\end{aligned}$$

Where $\rho^* = \left(\dfrac{\rho_w}{\rho_0}\right)$

$$T^* = \left(\frac{T}{T_0}\right)$$

ρ_w, density of water in kg m^{-3}

T, temperature in K

A_i, ρ_0, T_0, numerical constants given in Table A.1

Table A.1 Numerical values of coefficients in section A-I

A_1	7.62571E00
A_2	2.44003E02
A_3	-1.40569R02
A_4	2.77841E01
A_5	-9.62805E01
A_6	4.17909E01
A_7	-1.02099E01
A_8	-4.52059E01
A_9	8.46395E01
A_{10}	-3.58644E01
T_0	298.15 K
ρ_0	1000 kg m^{-3}

A-II. Ion Product of Water

Ion product (K_W) of water is calculated from the following correlation proposed by Marshall and Franck:

$$\log\left(K_W^*\right) = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \left(E + \frac{F}{T} + \frac{G}{T^2}\right)\log\left(\rho_w^*\right)$$

Where

$$K_W^* = K_W / \left(mol\right)^2 \left(kg\right)^{-2}, \qquad \rho_w^* = \rho_w / \left(g\right)\left(cm\right)^{-3}$$

and values for the parameters are

A = -4.098

B = -3245.2 K

C = 2.2362E05 K^2

D = -3.984E07 K^3

E = 13.957

F = -1262.3 K

G = 8.5641E05 K^2

Table A.2 Isobaric data of water at P = 24 MPa

T (C)	Pressure (MPa)	Density (kg/m^3)	Cp (J/mol*K)	Therm. Cond. (W/m*K)	Phase	log(Kw(mol/kg)^2)	ε
0.01	24	1011.7	74.118	0.57427	liquid	-14.83036255	88.93004
10.01	24	1010.8	74.104	0.5917	liquid	-14.42991646	85.00651
20.01	24	1008.9	74.148	0.60948	liquid	-14.07118158	81.2264
30.01	24	1006	74.222	0.62635	liquid	-13.74934898	77.58265
40.01	24	1002.4	74.309	0.64155	liquid	-13.45803329	74.09461
50.01	24	998.19	74.402	0.65472	liquid	-13.19336801	70.76187
60.01	24	993.37	74.499	0.66579	liquid	-12.9527465	67.57615
70.01	24	988.02	74.605	0.67487	liquid	-12.73335303	64.53599
80.01	24	982.19	74.723	0.68214	liquid	-12.53296448	61.63721
90.01	24	975.91	74.86	0.68781	liquid	-12.34979479	58.87409
100.01	24	969.2	75.02	0.6921	liquid	-12.18236274	56.24028
110.01	24	962.09	75.21	0.69518	liquid	-12.02930172	53.73039
120.01	24	954.58	75.432	0.69719	liquid	-11.88962743	51.33706
130.01	24	946.69	75.693	0.69824	liquid	-11.76233888	49.05469
140.01	24	938.42	75.995	0.6984	liquid	-11.64669618	46.87662
150.01	24	929.77	76.343	0.69773	liquid	-11.54205568	44.79652
160.01	24	920.75	76.741	0.69626	liquid	-11.44778389	42.80912
170.01	24	911.33	77.194	0.69399	liquid	-11.3636153	40.90691
180.01	24	901.52	77.709	0.69092	liquid	-11.28905547	39.0854
190.01	24	891.3	78.29	0.68704	liquid	-11.22389034	37.33855
200.01	24	880.66	78.947	0.68233	liquid	-11.16788664	35.66137
210.01	24	869.56	79.689	0.67677	liquid	-11.12108648	34.04753
220.01	24	857.98	80.527	0.67031	liquid	-11.08343457	32.49232
230.01	24	845.88	81.477	0.66291	liquid	-11.05507701	30.99032
240.01	24	833.23	82.556	0.6545	liquid	-11.03613736	29.53713
250.01	24	819.96	83.791	0.64503	liquid	-11.02710346	28.12671
260.01	24	806.01	85.211	0.6344	liquid	-11.02845547	26.7541
270.01	24	791.3	86.859	0.62252	liquid	-11.04090839	25.41389
280.01	24	775.73	88.793	0.60931	liquid	-11.0654339	24.10036
290.01	24	759.15	91.095	0.59467	liquid	-11.10353726	22.8062
300.01	24	741.4	93.885	0.57857	liquid	-11.15698525	21.52463
310.01	24	722.23	97.343	0.56101	liquid	-11.22854586	20.24601

T (C)	Pressure (MPa)	Density (kg/m^3)	Cp (J/mol*K)	Therm. Cond. (W/m*K)	Phase	log(Kw(mol/kg)^2)	ε
320.01	24	701.3	101.76	0.54206	liquid	-11.32214696	18.95853
330.01	24	678.1	107.63	0.52186	liquid	-11.44383744	17.64567
340.01	24	651.84	115.9	0.5005	liquid	-11.60330967	16.28343
350.01	24	621.11	128.65	0.4778	liquid	-11.81827321	14.83046
360.01	24	582.96	151.92	0.4528	liquid	-12.12687594	13.20263
370.01	24	528.7	212.64	0.42262	liquid	-12.64576353	11.15718
380.01	24	385.13	1140.9	0.40901	supercritical	-14.49987667	6.813174
390.01	24	178.16	328.12	0.1903	supercritical	-19.1089029	2.580786
400.01	24	148.53	194.54	0.14934	supercritical	-20.12707843	2.163999
410.01	24	132.61	147.27	0.13089	supercritical	-20.72903473	1.959533
420.01	24	121.87	122.09	0.12007	supercritical	-21.15668706	1.829418
430.01	24	113.86	106.18	0.113	supercritical	-21.4861071	1.736596
440.01	24	107.51	95.153	0.10813	supercritical	-21.75316795	1.665699
450.01	24	102.3	87.036	0.10466	supercritical	-21.97551014	1.609353
460.01	24	97.885	80.813	0.10218	supercritical	-22.16622804	1.562993
470.01	24	94.074	75.896	0.10042	supercritical	-22.33232101	1.524039
480.01	24	90.728	71.922	0.0992	supercritical	-22.47927542	1.490701
490.01	24	87.753	68.651	0.09839	supercritical	-22.61081519	1.461771
500.01	24	85.079	65.92	0.09793	supercritical	-22.72981273	1.436372
510.01	24	82.653	63.611	0.09773	supercritical	-22.83850279	1.41385
520.01	24	80.437	61.641	0.09776	supercritical	-22.93843481	1.393728
530.01	24	78.398	59.945	0.09798	supercritical	-23.03107259	1.375613
540.01	24	76.512	58.474	0.09835	supercritical	-23.11742605	1.359213
550.01	24	74.759	57.191	0.09886	supercritical	-23.19836039	1.344287
560.01	24	73.123	56.065	0.09947	supercritical	-23.27455625	1.330643
570.01	24	71.59	55.073	0.10018	supercritical	-23.34663796	1.318116
580.01	24	70.148	54.196	0.10096	supercritical	-23.41515438	1.30657
590.01	24	68.787	53.417	0.10181	supercritical	-23.48056051	1.295889
600.01	24	67.501	52.723	0.10272	supercritical	-23.54302455	1.285992

Table A.3 Isobaric data of water at P = 30 MPa

T (C)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	$\log(K_w(mol/kg)^2)$	ε
0.01	1014.5	73.712	1.7271	0.57754	liquid	-14.805381	89.192425
10.01	1013.5	73.781	1.2784	0.59461	liquid	-14.40653794	85.255163
20.01	1011.5	73.874	0.99155	0.61224	liquid	-14.04925604	81.461387
30.01	1008.6	73.979	0.79603	0.62907	liquid	-13.72792582	77.812966
40.01	1004.9	74.085	0.65624	0.64429	liquid	-13.43784881	74.311399
50.01	1000.7	74.189	0.55255	0.65751	liquid	-13.17346179	70.974699
60.01	995.84	74.293	0.47338	0.66865	liquid	-12.93345868	67.780776
70.01	990.51	74.401	0.41152	0.6778	liquid	-12.71416774	64.737363
80.01	984.7	74.519	0.36227	0.68516	liquid	-12.51384521	61.835258
90.01	978.47	74.652	0.32241	0.69094	liquid	-12.33048215	59.071065
100.01	971.82	74.807	0.28971	0.69534	liquid	-12.16275476	56.436786
110.01	964.77	74.988	0.26256	0.69853	liquid	-12.00937339	53.926268
120.01	957.35	75.2	0.23978	0.70067	liquid	-11.86913224	51.534307
130.01	949.55	75.446	0.22048	0.70186	liquid	-11.74125393	49.253092
140.01	941.38	75.732	0.20398	0.70218	liquid	-11.6249241	47.076628
150.01	932.86	76.059	0.18976	0.70167	liquid	-11.51935147	44.999892
160.01	923.96	76.434	0.17741	0.70036	liquid	-11.42419465	43.014895
170.01	914.7	76.858	0.16661	0.69827	liquid	-11.33881797	41.117334
180.01	905.06	77.339	0.15709	0.69539	liquid	-11.26294375	39.300696
190.01	895.04	77.88	0.14866	0.69171	liquid	-11.19620537	37.560113
200.01	884.61	78.489	0.14112	0.68723	liquid	-11.13851072	35.889309
210.01	873.75	79.173	0.13436	0.68191	liquid	-11.08974502	34.283053
220.01	862.45	79.942	0.12824	0.67573	liquid	-11.0497668	32.737062
230.01	850.68	80.807	0.12267	0.66864	liquid	-11.01863053	31.246311
240.01	838.39	81.785	0.11756	0.66061	liquid	-10.99659178	29.805155
250.01	825.54	82.892	0.11285	0.65156	liquid	-10.98388439	28.40896
260.01	812.09	84.153	0.10846	0.64144	liquid	-10.98079804	27.053521
270.01	797.96	85.598	0.10435	0.63018	liquid	-10.98799871	25.733126
280.01	783.08	87.268	0.10045	0.61769	liquid	-11.00615574	24.443128
290.01	767.35	89.218	0.09674	0.60391	liquid	-11.03627446	23.178052
300.01	750.64	91.526	0.09315	0.58881	liquid	-11.07973284	21.931769
310.01	732.78	94.3	0.08965	0.57241	liquid	-11.13841614	20.697257

T (C)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(K_w(mol/kg)^2)	ε
320.01	713.56	97.703	0.08618	0.55477	liquid	-11.21479455	19.466863
330.01	692.67	101.98	0.08271	0.53604	liquid	-11.31256599	18.230178
340.01	669.67	107.55	0.07916	0.51641	liquid	-11.4371672	16.973616
350.01	643.92	115.13	0.07546	0.49595	liquid	-11.59684462	15.678877
360.01	614.36	126.15	0.07149	0.47447	liquid	-11.80562872	14.316934
370.01	579.05	143.97	0.06705	0.45108	liquid	-12.09011435	12.836704
380.01	533.88	177.7	0.06176	0.4235	supercritical	-12.50965754	11.134813
390.01	468.72	258.34	0.05471	0.387	supercritical	-13.22709461	8.9799564
400.01	357.29	466.21	0.04393	0.33197	supercritical	-14.80096793	5.9327997
410.01	251.13	353.64	0.03541	0.24322	supercritical	-16.86198579	3.6735759
420.01	203.21	229.84	0.03253	0.19147	supercritical	-18.06614518	2.8545344
430.01	177.39	172.24	0.03144	0.16392	supercritical	-18.81072685	2.4650537
440.01	160.59	140.61	0.03099	0.14721	supercritical	-19.33590258	2.2312397
450.01	148.42	120.68	0.03085	0.13615	supercritical	-19.73726872	2.0716906
460.01	139.01	106.96	0.03088	0.12843	supercritical	-20.05973314	1.9541339
470.01	131.43	96.936	0.03101	0.12287	supercritical	-20.326898	1.8632103
480.01	125.11	89.301	0.03121	0.1188	supercritical	-20.55476892	1.7900996
490.01	119.73	83.3	0.03145	0.11581	supercritical	-20.75221999	1.7298524
500.01	115.07	78.47	0.03172	0.11362	supercritical	-20.92572428	1.6792007
510.01	110.95	74.508	0.03202	0.11205	supercritical	-21.0813968	1.6356984
520.01	107.29	71.208	0.03234	0.11097	supercritical	-21.22116282	1.5980581
530.01	104	68.424	0.03267	0.11027	supercritical	-21.34810463	1.5650743
540.01	101.01	66.051	0.03301	0.10989	supercritical	-21.46474994	1.5358399
550.01	98.274	64.009	0.03336	0.10977	supercritical	-21.57263638	1.5097306
560.01	95.76	62.239	0.03372	0.10985	supercritical	-21.67272467	1.4862916
570.01	93.436	60.695	0.03408	0.11011	supercritical	-21.76617217	1.4651132
580.01	91.277	59.34	0.03444	0.11052	supercritical	-21.85387213	1.4458741
590.01	89.262	58.145	0.0348	0.11104	supercritical	-21.93659682	1.4283099
600.01	87.375	57.086	0.03517	0.11167	supercritical	-22.01489773	1.4122132

Table A.4 Isobaric data of water at P = 36 MPa

T (C)	**Density (kg/m^3)**	**Cp (J/mol*K)**	**Viscosity (cP)**	**Therm. Cond. (W/m*K)**	**Phase**	**log(K_w (mol/kg)^2)**	**ε**
0.01	1017.4	73.329	1.7169	0.58078	liquid	-14.77957983	89.4632
10.01	1016.2	73.474	1.2743	0.5975	liquid	-14.38322162	85.503
20.01	1014	73.613	0.99027	0.615	liquid	-14.02822688	81.6867
30.01	1011.1	73.745	0.7962	0.63179	liquid	-13.70737865	78.0339
40.01	1007.4	73.868	0.65716	0.64702	liquid	-13.41771449	74.5278
50.01	1003.1	73.983	0.55386	0.66029	liquid	-13.15447459	71.1779
60.01	998.28	74.093	0.47489	0.67149	liquid	-12.91445203	67.9826
70.01	992.96	74.204	0.41312	0.68073	liquid	-12.69533767	64.9352
80.01	987.19	74.321	0.36389	0.68817	liquid	-12.49492639	62.0315
90.01	980.99	74.452	0.32403	0.69405	liquid	-12.31152056	59.2648
100.01	974.4	74.601	0.29131	0.69855	liquid	-12.14349773	56.6301
110.01	967.41	74.774	0.26413	0.70187	liquid	-11.98979656	54.1191
120.01	960.06	74.975	0.24132	0.70414	liquid	-11.84913829	51.7272
130.01	952.35	75.209	0.22199	0.70547	liquid	-11.72067275	49.4472
140.01	944.29	75.479	0.20545	0.70593	liquid	-11.60358642	47.2732
150.01	935.87	75.788	0.19121	0.70558	liquid	-11.49730726	45.1979
160.01	927.11	76.14	0.17883	0.70443	liquid	-11.40112586	43.2168
170.01	917.99	76.539	0.16801	0.70251	liquid	-11.31469729	41.3227
180.01	908.51	76.989	0.15848	0.69981	liquid	-11.23759398	39.5105
190.01	898.66	77.493	0.15003	0.69634	liquid	-11.16951865	37.7746
200.01	888.44	78.059	0.14249	0.69206	liquid	-11.11015221	36.1104
210.01	877.81	78.692	0.13572	0.68697	liquid	-11.05951901	34.5114
220.01	866.77	79.401	0.12961	0.68104	liquid	-11.01739422	32.9737
230.01	855.28	80.194	0.12404	0.67425	liquid	-10.98389513	31.4918
240.01	843.32	81.083	0.11895	0.66654	liquid	-10.95903559	30.0615
250.01	830.86	82.083	0.11426	0.65788	liquid	-10.94295029	28.6784
260.01	817.85	83.212	0.10991	0.64821	liquid	-10.93597689	27.3376
270.01	804.23	84.492	0.10584	0.63748	liquid	-10.93858936	26.0342
280.01	789.95	85.953	0.102	0.62561	liquid	-10.95124975	24.7643
290.01	774.94	87.633	0.09835	0.61257	liquid	-10.97465286	23.5233
300.01	759.08	89.585	0.09485	0.59833	liquid	-11.00999547	22.305

T (C)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(K_w (mol/kg)^2)	ε
310.01	742.28	91.877	0.09146	0.58288	liquid	-11.05836015	21.1055
320.01	724.38	94.609	0.08813	0.56631	liquid	-11.12157251	19.9182
330.01	705.17	97.921	0.08484	0.54875	liquid	-11.20212684	18.7356
340.01	684.4	102.02	0.08153	0.53039	liquid	-11.30321428	17.5498
350.01	661.71	107.23	0.07816	0.51141	liquid	-11.42952577	16.3505
360.01	636.57	114.08	0.07466	0.49184	liquid	-11.58816763	15.1229
370.01	608.24	123.51	0.07096	0.47141	liquid	-11.78970846	13.8489
380.01	575.45	137.37	0.06693	0.44927	supercritical	-12.0527267	12.4978
390.01	536.1	159.04	0.0624	0.42364	supercritical	-12.41039178	11.0234
400.01	486.99	193.71	0.05712	0.39165	supercritical	-12.9217839	9.36863
410.01	423.76	251.48	0.05083	0.35125	supercritical	-13.69355663	7.48968
420.01	348.61	290.57	0.04408	0.29998	supercritical	-14.80376059	5.57337
430.01	285.41	258.81	0.03915	0.24974	supercritical	-15.94108078	4.20596
440.01	242.72	208.93	0.03636	0.21202	supercritical	-16.84765419	3.40683
450.01	214.4	170.52	0.03488	0.18609	supercritical	-17.52512504	2.93201
460.01	194.48	144.11	0.03409	0.16824	supercritical	-18.0431373	2.62456
470.01	179.59	125.61	0.03368	0.1556	supercritical	-18.45455667	2.40924
480.01	167.94	112.14	0.0335	0.14642	supercritical	-18.79145628	2.24955
490.01	158.48	101.97	0.03347	0.13962	supercritical	-19.07501386	2.12569
500.01	150.59	94.056	0.03353	0.13454	supercritical	-19.31843947	2.02649
510.01	143.88	87.747	0.03366	0.13071	supercritical	-19.53035216	1.94513
520.01	138.06	82.615	0.03385	0.12784	supercritical	-19.7179573	1.87689
530.01	132.94	78.372	0.03407	0.12572	supercritical	-19.88599775	1.81871
540.01	128.39	74.815	0.03432	0.12417	supercritical	-20.03768242	1.7685
550.01	124.31	71.799	0.03459	0.12309	supercritical	-20.17559771	1.72471
560.01	120.61	69.216	0.03488	0.12239	supercritical	-20.30243505	1.68607
570.01	117.24	66.986	0.03518	0.12199	supercritical	-20.41937408	1.65176
580.01	114.15	65.046	0.03549	0.12183	supercritical	-20.52786903	1.62108
590.01	111.29	63.348	0.03582	0.12188	supercritical	-20.62963997	1.59338
600.01	108.65	61.853	0.03614	0.1221	supercritical	-20.72448284	1.56839

Table A.5 Isobaric data of water at P = 42 MPa

T (C)	**Density (kg/m^3)**	**Cp (J/mol*K)**	**Viscosity (cP)**	**Therm. Cond. (W/m*K)**	**Phase**	**$\log(K_w\ (mol/kg)^2)$**	**ε**
0.01	1020.2	72.968	1.7074	0.58398	liquid	-14.75473804	89.7236
10.01	1018.9	73.183	1.2705	0.60037	liquid	-14.35996717	85.7501
20.01	1016.6	73.364	0.98921	0.61774	liquid	-14.00641148	81.9205
30.01	1013.5	73.521	0.7965	0.6345	liquid	-13.68770111	78.2455
40.01	1009.8	73.661	0.65815	0.64975	liquid	-13.39843249	74.7351
50.01	1005.5	73.785	0.55521	0.66306	liquid	-13.13553277	71.3807
60.01	1000.7	73.9	0.47642	0.67433	liquid	-12.89564701	68.1825
70.01	995.38	74.013	0.41473	0.68364	liquid	-12.67678373	65.1304
80.01	989.64	74.13	0.36552	0.69117	liquid	-12.47635799	62.2244
90.01	983.48	74.257	0.32565	0.69714	liquid	-12.29283249	59.456
100.01	976.93	74.401	0.29291	0.70176	liquid	-12.12466335	56.8195
110.01	970.01	74.567	0.2657	0.70519	liquid	-11.97056849	54.3088
120.01	962.74	74.759	0.24285	0.70759	liquid	-11.8294211	51.9177
130.01	955.11	74.981	0.22348	0.70905	liquid	-11.70044473	49.6385
140.01	947.14	75.236	0.20692	0.70966	liquid	-11.58275234	47.4656
150.01	938.83	75.529	0.19264	0.70946	liquid	-11.47569827	45.3926
160.01	930.19	75.86	0.18024	0.70847	liquid	-11.37864537	43.4141
170.01	921.2	76.235	0.1694	0.70672	liquid	-11.2912463	41.5231
180.01	911.88	76.657	0.15985	0.7042	liquid	-11.2129248	39.7155
190.01	902.2	77.129	0.15138	0.70091	liquid	-11.14352546	37.9843
200.01	892.16	77.656	0.14383	0.69683	liquid	-11.08272497	36.3251
210.01	881.74	78.244	0.13706	0.69196	liquid	-11.03039368	34.7324
220.01	870.94	78.898	0.13095	0.68627	liquid	-10.98629836	33.2023
230.01	859.72	79.628	0.12539	0.67973	liquid	-10.95054464	31.7289
240.01	848.06	80.441	0.12031	0.67233	liquid	-10.92313326	30.3081
250.01	835.94	81.349	0.11564	0.66401	liquid	-10.90410674	28.9359
260.01	823.32	82.366	0.11131	0.65474	liquid	-10.89370363	27.6078
270.01	810.16	83.51	0.10727	0.64447	liquid	-10.89221248	26.3195
280.01	796.41	84.802	0.10348	0.63316	liquid	-10.9000544	25.0669
290.01	782.01	86.269	0.09989	0.62075	liquid	-10.91779356	23.8456
300.01	766.88	87.948	0.09646	0.60723	liquid	-10.94623225	22.6511
310.01	750.95	89.886	0.09315	0.59261	liquid	-10.98618775	21.4795

T (C)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(K$_w$ (mol/kg)^2)	ε
320.01	734.1	92.144	0.08993	0.57694	liquid	-11.03900749	20.3256
330.01	716.2	94.808	0.08678	0.56035	liquid	-11.10628921	19.1844
340.01	697.08	97.996	0.08364	0.54301	liquid	-11.19019299	18.05
350.01	676.51	101.87	0.08049	0.52511	liquid	-11.2937213	16.9153
360.01	654.21	106.69	0.07729	0.5068	liquid	-11.4207914	15.7727
370.01	629.78	112.8	0.07399	0.48804	liquid	-11.57713674	14.6121
380.01	602.68	120.81	0.07055	0.46847	supercritical	-11.77097952	13.4211
390.01	572.14	131.69	0.06688	0.44729	supercritical	-12.01477635	12.1837
400.01	537.07	146.62	0.0629	0.42314	supercritical	-12.32783448	10.8798
410.01	496.33	166.31	0.05857	0.3944	supercritical	-12.73627668	9.49831
420.01	449.24	191.2	0.05388	0.3605	supercritical	-13.27081509	8.05405
430.01	396.49	215.56	0.04903	0.32209	supercritical	-13.95754573	6.60816
440.01	344.42	217.56	0.04467	0.28217	supercritical	-14.73952586	5.34249
450.01	300.53	201.1	0.0414	0.24748	supercritical	-15.49397897	4.39432
460.01	266.47	177.72	0.03919	0.21972	supercritical	-16.15176586	3.73256
470.01	240.65	155.59	0.03777	0.19846	supercritical	-16.69937061	3.2739
480.01	220.81	137.38	0.03688	0.18241	supercritical	-17.15222627	2.94677
490.01	205.18	123	0.03634	0.17029	supercritical	-17.53018265	2.70465
500.01	192.53	111.68	0.03602	0.16109	supercritical	-17.85053697	2.51891
510.01	182.05	102.67	0.03587	0.15406	supercritical	-18.12610602	2.37208
520.01	173.19	95.395	0.03583	0.14867	supercritical	-18.3664837	2.25305
530.01	165.56	89.439	0.03587	0.14453	supercritical	-18.57915702	2.15439
540.01	158.92	84.496	0.03598	0.14136	supercritical	-18.76842965	2.07147
550.01	153.05	80.343	0.03613	0.13895	supercritical	-18.93925149	2.00055
560.01	147.81	76.818	0.03632	0.13716	supercritical	-19.09459419	1.93917
570.01	143.1	73.798	0.03653	0.13585	supercritical	-19.23651964	1.8856
580.01	138.83	71.189	0.03677	0.13494	supercritical	-19.36717708	1.83838
590.01	134.92	68.919	0.03703	0.13435	supercritical	-19.48872217	1.79631
600.01	131.34	66.932	0.0373	0.13401	supercritical	-19.60143644	1.75878

Table A.6 Isothermal data for water at T = 650^{o}C

Pressure (MPa)	Density (kg/m^3)	Cp (J/g*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(Kw (mol/kg)^2)
0	0	2.236	0.034596	0.086518	vapor	
1	2.3557	2.2548	0.034634	0.087099	vapor	-43.1264
2	4.7289	2.274	0.034675	0.087705	vapor	-39.0121
3	7.1198	2.2934	0.034718	0.088336	vapor	-36.5963
4	9.5288	2.3133	0.034765	0.088992	vapor	-34.8756
5	11.956	2.3335	0.034814	0.089674	vapor	-33.5359
6	14.402	2.354	0.034866	0.090382	vapor	-32.437
7	16.867	2.3749	0.034921	0.091116	vapor	-31.5042
8	19.352	2.3962	0.034978	0.091877	vapor	-30.6927
9	21.856	2.4179	0.035039	0.092664	vapor	-29.9743
10	24.38	2.4399	0.035103	0.093478	vapor	-29.3291
11	26.924	2.4623	0.035169	0.094319	vapor	-28.7431
12	29.488	2.485	0.035239	0.095188	vapor	-28.206
13	32.074	2.5082	0.035311	0.096085	vapor	-27.7097
14	34.68	2.5317	0.035386	0.097009	vapor	-27.2485
15	37.308	2.5555	0.035465	0.097962	vapor	-26.8173
16	39.957	2.5798	0.035546	0.098943	vapor	-26.4123
17	42.628	2.6044	0.035631	0.099953	vapor	-26.0302
18	45.321	2.6294	0.035719	0.10099	vapor	-25.6686
19	48.037	2.6548	0.035809	0.10206	vapor	-25.3249
20	50.775	2.6805	0.035903	0.10316	vapor	-24.9977
21	53.536	2.7066	0.036	0.10428	vapor	-24.685
22	56.319	2.733	0.036101	0.10544	vapor	-24.3858
23	59.126	2.7598	0.036204	0.10663	vapor	-24.0987
23	59.126	2.7598	0.036204	0.10663	supercritical	-24.0987
23	59.126	2.7598	0.036204	0.10663	supercritical	-24.0987
24	61.956	2.787	0.036311	0.10785	supercritical	-23.8226
25	64.81	2.8145	0.036421	0.10909	supercritical	-23.5567
26	67.686	2.8424	0.036534	0.11037	supercritical	-23.3004
27	70.587	2.8706	0.03665	0.11168	supercritical	-23.0526
28	73.511	2.8991	0.03677	0.11302	supercritical	-22.813
29	76.459	2.9279	0.036893	0.11439	supercritical	-22.5808

Pressure (MPa)	Density (kg/m3)	Cp (J/g*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(Kw (mol/kg)^2)
30	79.431	2.957	0.037019	0.11579	supercritical	-22.3557
31	82.427	2.9865	0.037149	0.11721	supercritical	-22.1371
32	85.447	3.0162	0.037282	0.11867	supercritical	-21.9247
33	88.491	3.0462	0.037419	0.12016	supercritical	-21.718
34	91.558	3.0765	0.037558	0.12168	supercritical	-21.5168
35	94.649	3.1071	0.037702	0.12323	supercritical	-21.3208
36	97.764	3.1379	0.037848	0.12481	supercritical	-21.1296
37	100.9	3.1689	0.037998	0.12642	supercritical	-20.9432
38	104.06	3.2001	0.038151	0.12806	supercritical	-20.7611
39	107.25	3.2315	0.038308	0.12972	supercritical	-20.5829
40	110.46	3.2631	0.038468	0.13141	supercritical	-20.4088
41	113.69	3.2948	0.038631	0.13313	supercritical	-20.2386
42	116.94	3.3267	0.038798	0.13488	supercritical	-20.0722
43	120.22	3.3587	0.038968	0.13665	supercritical	-19.9089
44	123.52	3.3909	0.039141	0.13845	supercritical	-19.749
45	126.84	3.4231	0.039318	0.14027	supercritical	-19.5924
46	130.18	3.4553	0.039498	0.14212	supercritical	-19.4389
47	133.54	3.4876	0.039681	0.14399	supercritical	-19.2885
48	136.92	3.5199	0.039867	0.14588	supercritical	-19.1409
49	140.32	3.5522	0.040057	0.1478	supercritical	-18.9961
50	143.74	3.5845	0.04025	0.14973	supercritical	-18.8539

Table A.7 Isothermal data for water at T = 400^{o}C

Pressure (MPa)	**Density (kg/m^3)**	**Cp (J/mol*K)**	**Viscosity (cP)**	**Therm. Cond. (W/m*K)**	**Phase**	**log(K$_w$ (mol/kg)^2)**
0	0	37.175	0.02445	0.05467	vapor	
1	3.2615	38.36	0.02442	0.05562	vapor	-43.29785638
2	6.6131	39.657	0.0244	0.05662	vapor	-39.00870342
3	10.062	41.077	0.02438	0.05769	vapor	-36.4619452
4	13.618	42.633	0.02437	0.05884	vapor	-34.62565292
5	17.29	44.336	0.02437	0.06006	vapor	-33.17703949
6	21.088	46.205	0.02437	0.06138	vapor	-31.9721109
7	25.026	48.257	0.02439	0.0628	vapor	-30.93322741
8	29.117	50.514	0.02441	0.06435	vapor	-30.01451293
9	33.378	53.006	0.02444	0.06604	vapor	-29.18579746
10	37.827	55.762	0.02449	0.06788	vapor	-28.42655081
11	42.486	58.824	0.02454	0.06992	vapor	-27.72176104
12	47.38	62.24	0.02461	0.07217	vapor	-27.06021008
13	52.54	66.069	0.0247	0.07468	vapor	-26.43294857
14	58.003	70.387	0.02481	0.0775	vapor	-25.83271712
15	63.812	75.291	0.02493	0.08068	vapor	-25.25356188
16	70.021	80.903	0.02508	0.08431	vapor	-24.69013809
17	76.697	87.388	0.02526	0.08846	vapor	-24.13755475
18	83.924	94.964	0.02547	0.09326	vapor	-23.5911507
19	91.81	103.93	0.02573	0.09886	vapor	-23.04619951
20	100.5	114.71	0.02603	0.10547	vapor	-22.49744434
21	110.18	127.93	0.02641	0.11337	vapor	-21.93945899
22	121.13	144.5	0.02687	0.12291	vapor	-21.3645365
23	133.73	165.92	0.02745	0.13465	vapor	-20.76407118
23	133.73	165.92	0.02745	0.13465	supercritical	-20.76407118
23	133.73	165.92	0.02745	0.13465	supercritical	-20.76407118
24	148.55	194.61	0.02819	0.14937	supercritical	-20.12634763
25	166.54	234.78	0.02917	0.16824	supercritical	-19.43270788
26	189.21	293.61	0.03054	0.19303	supercritical	-18.65831676
27	219.12	380.44	0.03253	0.22589	supercritical	-17.76778681
28	259.44	484.99	0.03551	0.26633	supercritical	-16.74289086
29	309.07	539.75	0.0396	0.3064	supercritical	-15.68076022

Pressure (MPa)	**Density (kg/m^3)**	**Cp (J/mol*K)**	**Viscosity (cP)**	**Therm. Cond. (W/m*K)**	**Phase**	**log(K_w (mol/kg)^2)**
30	357.43	466.02	0.04394	0.33204	supercritical	-14.7986662
31	394.52	373.19	0.04748	0.34707	supercritical	-14.19958553
32	422.45	306.78	0.05027	0.35882	supercritical	-13.78453692
33	443.84	261.12	0.05247	0.36853	supercritical	-13.48482734
34	460.86	230.56	0.05427	0.37707	supercritical	-13.25649309
35	474.97	209.3	0.05579	0.38474	supercritical	-13.0735029
36	487.04	193.67	0.05712	0.39169	supercritical	-12.92123255
37	497.63	181.61	0.05831	0.39802	supercritical	-12.79070961
38	507.06	171.95	0.05938	0.40383	supercritical	-12.67680082
39	515.57	163.99	0.06036	0.40918	supercritical	-12.57580907
40	523.34	157.3	0.06127	0.41416	supercritical	-12.48504456
41	530.49	151.57	0.06212	0.41881	supercritical	-12.4027053
42	537.11	146.6	0.06291	0.42317	supercritical	-12.32745298
43	543.28	142.26	0.06366	0.42729	supercritical	-12.25814645
44	549.06	138.42	0.06436	0.4312	supercritical	-12.19393109
45	554.49	135.01	0.06503	0.43491	supercritical	-12.13421709
46	559.63	131.95	0.06568	0.43846	supercritical	-12.07822856
47	564.51	129.19	0.06629	0.44186	supercritical	-12.02554598
48	569.14	126.69	0.06688	0.44513	supercritical	-11.97598165
49	573.56	124.41	0.06744	0.44828	supercritical	-11.92904014
50	577.79	122.32	0.06799	0.45132	supercritical	-11.884454

Table A.8 Isothermal data for water at T = 386^{o}C

Pressure (MPa)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(K$_w$ (mol/kg)^2)
0	0	37.01	0.02387	0.05302	vapor	
1	3.3346	38.311	0.02383	0.05403	vapor	-43.3553783
2	6.7697	39.751	0.0238	0.0551	vapor	-39.04600627
3	10.315	41.346	0.02378	0.05625	vapor	-36.48302249
4	13.981	43.11	0.02376	0.05748	vapor	-34.63233323
5	17.78	45.065	0.02375	0.0588	vapor	-33.16946183
6	21.727	47.234	0.02375	0.06023	vapor	-31.94937367
7	25.837	49.647	0.02375	0.06179	vapor	-30.89499943
8	30.13	52.338	0.02377	0.0635	vapor	-29.95952974
9	34.628	55.352	0.0238	0.06538	vapor	-29.11274541
10	39.358	58.743	0.02384	0.06746	vapor	-28.3335413
11	44.352	62.582	0.0239	0.06979	vapor	-27.60654175
12	49.648	66.957	0.02397	0.07242	vapor	-26.92006286
13	55.295	71.986	0.02406	0.0754	vapor	-26.26447497
14	61.352	77.825	0.02418	0.07882	vapor	-25.63188588
15	67.896	84.688	0.02432	0.08279	vapor	-25.01509507
16	75.027	92.878	0.0245	0.08745	vapor	-24.40730166
17	82.878	102.84	0.02472	0.093	vapor	-23.80163417
18	91.632	115.23	0.02499	0.09972	vapor	-23.19055453
19	101.56	131.15	0.02533	0.10803	vapor	-22.56451425
20	113.05	152.46	0.02578	0.11856	vapor	-21.91223665
21	126.78	182.71	0.02636	0.13239	vapor	-21.2146646
22	143.93	229.65	0.02718	0.15151	vapor	-20.44253756
23	166.99	313.94	0.02842	0.18024	vapor	-19.53814752
23	166.99	313.94	0.02842	0.18024	supercritical	-19.53814752
23	166.99	313.94	0.02842	0.18024	supercritical	-19.53814752
24	202.77	510.53	0.03064	0.23057	supercritical	-18.3566621
25	278.35	1131.8	0.03629	0.3384	supercritical	-16.42864154
26	386.94	682.14	0.04611	0.37504	supercritical	-14.42404139
27	436.16	401.32	0.05109	0.38116	supercritical	-13.69533198
28	464.16	295.13	0.05406	0.38843	supercritical	-13.31667312
29	483.49	244.74	0.05618	0.39596	supercritical	-13.06836493

Pressure (MPa)	**Density (kg/m^3)**	**Cp (J/mol*K)**	**Viscosity (cP)**	**Therm. Cond. (W/m*K)**	**Phase**	**log(K_w (mol/kg)^2)**
30	498.43	215.48	0.05785	0.40304	supercritical	-12.88315899
31	510.73	195.96	0.05926	0.40949	supercritical	-12.73480012
32	521.24	181.76	0.06048	0.41534	supercritical	-12.61083555
33	530.44	170.86	0.06157	0.42069	supercritical	-12.50435699
34	538.65	162.18	0.06256	0.42562	supercritical	-12.41088438
35	546.07	155.07	0.06346	0.43021	supercritical	-12.32762371
36	552.85	149.12	0.06429	0.4345	supercritical	-12.25252784
37	559.11	144.07	0.06507	0.43854	supercritical	-12.18400479
38	564.92	139.71	0.06581	0.44237	supercritical	-12.12109054
39	570.36	135.91	0.0665	0.44602	supercritical	-12.0627667
40	575.47	132.56	0.06716	0.4495	supercritical	-12.00848536
41	580.29	129.58	0.06778	0.45284	supercritical	-11.95772452
42	584.86	126.91	0.06838	0.45605	supercritical	-11.9099844
43	589.21	124.49	0.06895	0.45915	supercritical	-11.86488777
44	593.36	122.31	0.06951	0.46215	supercritical	-11.8221738
45	597.33	120.31	0.07004	0.46504	supercritical	-11.78159115
46	601.13	118.47	0.07055	0.46786	supercritical	-11.74299817
47	604.79	116.78	0.07105	0.47059	supercritical	-11.70605698
48	608.31	115.22	0.07153	0.47325	supercritical	-11.67073913
49	611.7	113.76	0.072	0.47585	supercritical	-11.6369183
50	614.98	112.41	0.07246	0.47838	supercritical	-11.60437283

Table A.9 Isothermal data for water at T = 374°C

Pressure (MPa)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(Kw (mol/kg)^2)
0	0	36.869	0.02338	0.05161	vapor	
1	3.4001	38.284	0.02333	0.05269	vapor	-43.41136384
2	6.9109	39.867	0.02329	0.05383	vapor	-39.08295628
3	10.544	41.637	0.02325	0.05505	vapor	-36.50495075
4	14.312	43.617	0.02323	0.05636	vapor	-34.6404127
5	18.232	45.836	0.02321	0.05778	vapor	-33.16314215
6	22.32	48.327	0.0232	0.05933	vapor	-31.92859547
7	26.598	51.133	0.02321	0.06103	vapor	-30.85852064
8	31.091	54.308	0.02322	0.06291	vapor	-29.9060424
9	35.83	57.921	0.02324	0.065	vapor	-29.04031123
10	40.851	62.061	0.02328	0.06734	vapor	-28.24000626
11	46.201	66.849	0.02334	0.07001	vapor	-27.48898206
12	51.937	72.445	0.02342	0.07306	vapor	-26.77481726
13	58.135	79.075	0.02352	0.07661	vapor	-26.08685348
14	64.893	87.066	0.02365	0.08081	vapor	-25.4157603
15	72.347	96.909	0.02382	0.08584	vapor	-24.7522197
16	80.689	109.38	0.02403	0.09201	vapor	-24.08627448
17	90.203	125.82	0.02431	0.09979	vapor	-23.40609749
18	101.34	148.69	0.02468	0.10994	vapor	-22.69566424
19	114.92	183.35	0.0252	0.12393	vapor	-21.92825573
20	132.56	244.16	0.02597	0.14501	vapor	-21.05683715
21	158.85	391.47	0.0273	0.18364	vapor	-19.95275909
22	232.51	2703.1	0.03205	0.39813	vapor	-17.62790723
23	469.23	407.96	0.05415	0.40406	vapor	-13.34304165
23	469.23	407.96	0.05415	0.40406	supercritical	-13.34304165
23	469.23	407.96	0.05415	0.40406	supercritical	-13.34304165
24	495.97	279.53	0.05713	0.40813	supercritical	-13.00483164
25	513.45	230.58	0.05914	0.41461	supercritical	-12.79346124
26	526.8	203.17	0.0607	0.42078	supercritical	-12.63682271
27	537.73	185.16	0.06201	0.42641	supercritical	-12.51150607
28	547.07	172.23	0.06315	0.43158	supercritical	-12.40642145
29	555.25	162.41	0.06416	0.43634	supercritical	-12.31585136

Pressure (MPa)	Density (kg/m^3)	Cp (J/mol*K)	Viscosity (cP)	Therm. Cond. (W/m*K)	Phase	log(Kw (mol/kg)^2)
30	562.57	154.65	0.06508	0.44078	supercritical	-12.23592746
31	569.21	148.32	0.06592	0.44495	supercritical	-12.16432264
32	575.3	143.05	0.0667	0.44888	supercritical	-12.09937954
33	580.94	138.57	0.06744	0.45261	supercritical	-12.03984544
34	586.2	134.71	0.06813	0.45617	supercritical	-11.9848411
35	591.13	131.34	0.06878	0.45958	supercritical	-11.93373385
36	595.78	128.36	0.0694	0.46286	supercritical	-11.88591836
37	600.18	125.7	0.06999	0.46601	supercritical	-11.841016
38	604.36	123.31	0.07056	0.46906	supercritical	-11.79866263
39	608.35	121.15	0.07111	0.47201	supercritical	-11.75850678
40	612.16	119.18	0.07164	0.47487	supercritical	-11.72040755
41	615.82	117.38	0.07215	0.47766	supercritical	-11.68403093
42	619.33	115.73	0.07264	0.48036	supercritical	-11.64934768
43	622.71	114.19	0.07312	0.483	supercritical	-11.61613427
44	625.97	112.77	0.07358	0.48558	supercritical	-11.58427039
45	629.11	111.45	0.07403	0.4881	supercritical	-11.55373592
46	632.16	110.21	0.07447	0.49057	supercritical	-11.52422221
47	635.11	109.06	0.0749	0.49298	supercritical	-11.49581132
48	637.97	107.97	0.07532	0.49535	supercritical	-11.46839291
49	640.75	106.94	0.07573	0.49767	supercritical	-11.441859
50	643.45	105.98	0.07613	0.49995	supercritical	-11.41619863

Name: Pranay Namilakonda Date of Degree: December, 2005

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: DEGRADATION KINETICS OF ORGANIC AMINES IN SUPERCRITICAL WATER

Pages in Study: 97 Candidate for Degree of Master of Science

Major Field: Chemical Engineering

Scope and Method of Study:

Organic amines are widely used in hydrothermal systems operating at sub and near critical conditions as potential pH stabilizing agents. This report investigates the feasibility of their application in hydrothermal systems operating beyond critical point of water. Reaction kinetics of organic amine degradation plays a key role in evaluating their stability, basicity and volatility in supercritical water. A thorough literature review indicates that organic compounds in supercritical water decompose through pyrolysis and hydrolysis mechanisms. Pyrolysis mechanism is favored at low water densities and hydrolysis at high water densities, density being specific to organic compound. The reaction rate in hydrolysis pathway is significantly altered by solvent properties like ionic product and dielectric constant.

Findings and Conclusions:

Organic amines have the potential to serve as pH stabilizing agents in supercritical hydrothermal systems. Better prediction of degradation kinetics in hydrolysis pathway needs a modification in the kinetic equation by incorporating the effects of solvent properties.

ADVISOR'S APPROVAL Gary L. Foutch

VITA

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